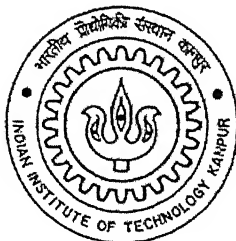


Heterogeneous Catalytic Reactions of Alkanes in Presence of Supported Zirconium Complex Catalyst

*A thesis submitted in
partial fulfillment of the requirements
for the degree of*

Master of Technology

By
Anisia K.S



To the
**DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR**

July, 2002

To My Parents....

पुरुषोत्तम काशीनाथ केनकर पुस्तकालय

भारतीय प्रौद्योगिकी संस्थान कानपुर

अवधि क्र० A 141808



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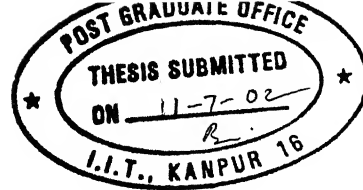
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I'm deeply indebted to my parents and my sister, Jasu for their love inspiration and support throughout the years. Their blessings and prayers continue to be my strength.

July, 2002.

Anisia K.S.



CERTIFICATE

This is to certify that the work contained in the thesis entitled *“Heterogeneous Catalytic Reactions of Alkanes in Presence of Supported Zirconium Complex Catalyst ”*, by *Anisia K.S*, has been carried out under my supervision and this work has not been submitted elsewhere for a degree.

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11th July, 2002

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Abstract

In this work we have synthesized a zirconium metal complex with [1,4-bis (salicylidene amino)-phenylene] and devised a method of molecularly binding it with silica gel as well as alumina supports. The heterogeneous catalyst, thus formed, has been used to study the reforming (n-hexane) and oxidation (n-heptane and cyclohexane) reactions for alkanes. We have also used this metal complex catalyst for depolymerization of HDPE. The use of this catalyst reduces the reaction temperature (reforming of n-hexane at 120°C as against 350°C for Pt/Al₂O₃, oxidation of n-heptane at 200°C as against 250°C for SAPO molecular sieve, depolymerization of HDPE at 335°C as against 430°C for zeolite). In presence of this catalyst, there is a considerable increase in conversion (77% conversion for n-hexane as against 85% for Pt/Al₂O₃, 21% conversion for cyclohexane at 200°C as against 4% conversion for homogeneous cobalt salts, 79% conversion for n-heptane as against 35% for SAPO catalyst). The catalyst also demonstrates high specificity when compared to the already existing processes (no benzene, 2,2-DMB and 2,3-DMB in the reformation of n-hexane, cyclohexanol with 72% selectivity and cyclohexene with 11% selectivity is formed on cyclohexane oxidation as opposed to the formation of cyclohexanol with 52% selectivity and cyclohexanone with 33% selectivity for homogeneous cobalt salts, heptane oxidation gives 2-MP, MCP 4-methyl,1-pentene, cyclohexanone and toluene as opposed to the formation of furans, pyrans, heptanones and heptanol for SAPO molecular sieve).

Chapter 1

Introduction

The quantity of plastic waste discarded each year is constantly on the rise. Since these are non biodegradable, it has been of late causing serious disposal problems ¹. Some of the methods adopted for disposal are landfilling, incineration and plastic recycling and these suffer from the following drawbacks ².

1. When plastics are dumped, the original material is destroyed and there is no recovery of energy. This method of disposal is not preferred because the landfill space is getting reduced with time.
2. Plastics can be incinerated with energy recovery in municipal waste incinerators or steel plants. However during this process the original material is lost and there is emission of carcinogens such as dioxins (polychlorinated dibenzodioxins), furans (polychlorinated dibenzofurans) and poisonous gases like phosgene.

Plastics are recycled and the technology is currently based on pelletization and moulding into low grade plastics. The main disadvantage of this technique is that the recycled material possesses poor mechanical strength and colour qualities and hence have a lower market value.

It is desirable to convert plastic materials into their original monomers, but complete monomer recovery is possible only in few specific cases. Attempts have been made to recover monomers from polymers such as polymethylmetacrylate (PMMA), polystyrene (PS) and polytetrafluoroethylene (PTFE). Monomer recovery from PMMA has been high but never more than 97% while that from PS is about 70%. Condensation polymers such as

polyamides and polyesters may yield monomers by chemolysis (hydrolysis, glycolysis etc) and the recovery in general has been high. In contrast addition polymers, such as polyolefins cannot be easily depolymerized into their original monomers.

Waste plastics can be converted into fuel oil and valuable chemicals by using degradation technologies. Thermal and catalytic degradation of plastics are two kind of chemical processes and the main drawbacks of the former are

- (a) Wide product distribution and
- (b) Requirement of high temperatures, typically between 500⁰C to 900⁰C.

Catalytic degradation occurs at lower temperatures and by choosing appropriate catalysts and the type of reactors both product yield and product distribution can be controlled potentially leading to a cost effective process with more valuable products. The reaction rate also increases significantly and the rate of degradation of polypropylene was reported to be approximately four times faster than that of non-catalytic thermal degradation³. More than 70% of the plastics currently produced have been composed of polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyvinylchloride (PVC). Among these polymers PE and PP have been intended to be converted into fuel oils, while PS has been expected to be recycled into styrene monomer. In the case of PVC, the main problem is how to eliminate the chloride ion.

The tendency of the different polymers to decompose is found to decrease according to the series polyisobutadiene > low density polyethylene > polypropylene > high density polyethylene. Experiments have shown that in the absence of any catalyst degradation of high density polyethylene (HDPE) give high gas yields⁴. In presence of silica-alumina catalyst (catalyst/ feed HDPE ratio = 1:1) the feed gave about 52 wt % of

gas and oil at 320⁰C with a reaction time of 60 minutes ⁵. At a temperature of 420⁰C-450⁰C in presence of hydrogen gas at 500 psig – 2000 psig liquid yield was found to increase to 80% over ZrO₂/SO₄²⁻ catalyst ⁶. In an alternate study, Ni/ZrO₂/SO₄²⁻ and Pt/ZrO₂/SO₄²⁻ catalysts gave 99wt % conversion with 19- 30 wt % gas yield at 375⁰C ⁷. The zeolite HZSM-5 was also used as a catalyst for depolymerization of HDPE with tetralin as the solvent in presence of H₂ (800 psig) at 430⁰C and in this case 98 wt % conversion was reached for a reaction time of 60 minutes ⁸. The ratio of HZSM-5 to HDPE was 1:100 and the ratio of tetralin to HDPE was 3:2.

Solid acid catalysts are commonly used in the study of catalytic degradation of plastics due to their wide spread use in the petroleum industry and due to their ability to cleave carbon – carbon bonds. Uemichi et al. ⁹ studied the catalytic degradation of PE in presence of catalysts such as Al₂O₃, Pt/Al₂O₃, SiO₂-Al₂O₃, Pt/SiO₂-Al₂O₃, C, Pt/C. It was found that when reforming catalyst (Pt/SiO₂-Al₂O₃) was used there was considerable increase in the yield of aromatics at the expense of normal and isoalkanes. When Pt impregnated on activated carbon was used as catalyst the aromatic yield was 50% of the feed, due to the combination of cracking and dehydrocyclization activities of the catalyst.

Ding et al. ¹⁰ studied the degradation of HDPE as well as post consumer plastics (CP#2) into liquid fuel products using TiCl₃ (conventionally used for polymerization of ethylene to HDPE) and HZSM-5 (a conventional cracking catalyst used in the petroleum industry) as catalysts in the temperature range 400⁰C – 430⁰C. Mainly oil products were obtained over TiCl₃ catalyst while large amount of gas was produced over HZSM-5 catalyst and both the yields increased with temperature. TiCl₃ catalyzed recombination and disproportionation reactions while HZSM-5 catalyzed cyclization and aromatization

reactions. The gaseous products contain mostly $C_1 - C_6$ hydrocarbons and the oil products consisted of mostly $C_5 - C_{27}$ hydrocarbons. Luo et al.¹¹ studied the catalytic degradation of HDPE and PP into liquid fuel in a powder particle fluidized bed using F9, a zeolite catalyst with Na_2O inclusions and highly porous silica-alumina catalyst. Batch experiments were conducted for 1 hour in the temperature range of $400^{\circ}C - 550^{\circ}C$ and found that depolymerization of HDPE and PP over silica-alumina produced higher yield of liquid products and more valuable gaseous products. In the liquid phase, C_6 is the main component for silica-alumina catalyst while C_7 is the main component for F9 catalyst, with a narrow distribution. The gaseous products formed over silica-alumina catalyst contained ethylene and propylene as the major components while with F9 catalyst methane was formed in large amounts.

Azharuddin et al.¹² studied the degradation of HDPE and PP into liquid hydrocarbons using non- acidic mesoporous silica catalyst denoted by FSM. It was found that when compared with thermal degradation, non acidic FSM catalyst accelerated the initial rate of degradation, increased the liquid product yield and promoted degradation into lower molecular weight products. Aguado et al.¹³ studied the catalytic conversion of polyolefins into fuels over β -zeolite catalyst which has large pores, possesses a three dimensional structure of interconnected channels with two different pore sizes and has high thermal stability. It was found that the β -zeolite synthesized from amorphous silica-alumina xerogels degrades all the polyolefins with high conversion and good selectivity towards $C_5 - C_{12}$ hydrocarbons, heavier products being formed only in minor amounts.

Manos et al.¹⁴ studied the catalytic degradation of HDPE on an ultrastable Y-zeolite and found that the depolymerization occurred at a much lower temperatures than

pure thermal degradation. The product consists of $C_3 - C_{15}$ hydrocarbons, isobutane and isopentane being the main components in the gaseous phase and the liquid phase was found to be alkane rich. Fernandes et al.¹⁵ studied the degradation of HDPE in presence of silicoaluminophosphate (SAPO-37) catalyst and found that the product formed were distributed between carbon number C_2 to C_{12} . Griekan et al.¹⁶ studied the thermal and catalytic degradation of PE (LDPE and HDPE) and determined the properties of solid waxy product obtained. The different types of catalyst used were HZSM-5 and HY zeolites, amorphous silica-alumina, activated carbon, palladium-charcoal powder and mesoporous alumino silicate materials (MCM-41) with and without palladium. It was found that the product obtained from HDPE had a higher homogeneity than that from LDPE but higher reaction temperatures were required. For LDPE degradation best results were obtained with MCM-41 catalyst and the product formed was of high quality. Polymer cracking occurs through random scission mechanism and the hydrogen transfer mechanism reduces the olefins formed in the products.

Aguado et al.¹⁷ studied the catalytic conversion of mixture of polyolefins consisting of PP, HDPE and LDPE using HMCM-41 (mesoporous zeolite) and HZSM-5 (nanosized zeolite) catalyst. Different product distributions were obtained with these two catalysts and this has been related to the different cracking mechanism as follows. HZSM-5 has high external surface area and strong acid sites, which promotes end chain scission reactions leading to the formation of light hydrocarbons ($C_3 - C_6$). HMCM-41 has large pores and mild acidity which promotes random scission reactions leading to the formation of heavier products ($C_5 - C_{12}$ and $C_{13} - C_{22}$). Sakata et al.¹⁸ studied the catalytic degradation of municipal waste plastics, which consists of PE, PP, PS, PVC, acrylonitrile-

butadiene-styrene (ABS) and polyethyleneterephthalate (PET) into fuel using silica-alumina catalysts. It was found that PVC and PET lead to the formation of large amount of solid residues and the carbon number varied from C₅ to C₁₅ in the liquid products.

Lee et al.¹⁹ studied the catalytic degradation of PS over natural zeolite (HNZ) at 400°C and compared its performance on HZSM-5, silica-alumina, and also with thermal degradation. HNZ was as effective as HZSM-5 and produced liquid products with carbon numbers in the range C₅ – C₁₂ while with silica-alumina the yield of ethylbenzene was highest and styrene the lowest. They found that at higher temperatures, for HNZ there was an increase in the selectivity for styrene and the yield of styrene dimers were low. Ukei et al.²⁰ studied the catalytic degradation of PS into styrene in presence of solid acids and bases as catalysts and they found that solid bases were more effective catalysts. Zhang et al.²¹ found that solid bases such as BaO and K₂O showed pronounced catalytic activity in converting waste PS into styrene monomer.

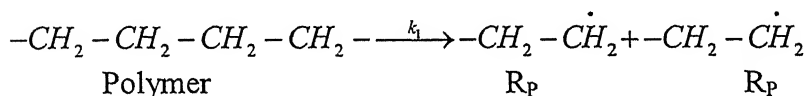
Jalil²² studied the catalytic degradation of HDPE at 420°C and atmospheric pressure under batch conditions using mesoporous MCM-41 material, tungstophosphoric acid (H₂PW₁₂O₄₀), water and methanol impregnated tungstophosphoric acid over MCM-41 material. It was found that MCM-41 and tungstophosphoric acid did not show any catalytic behavior but the methanol and water impregnated tungstophosphoric acid promoted degradation of HDPE. Sakata et al.²³ found that catalyst possessing acid sites such as zeolite ZSM-5 accelerated the degradation of PP and PE into gases and resulted in low liquid yields.

All mechanisms for depolymerization of polymers proposed in literature have been through free radical mechanism, carboniumion mechanism and carbanion mechanism.

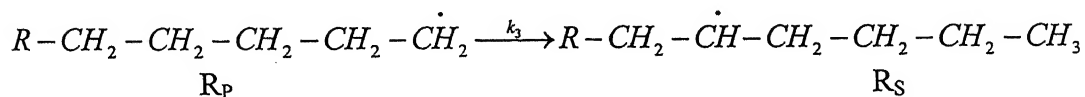
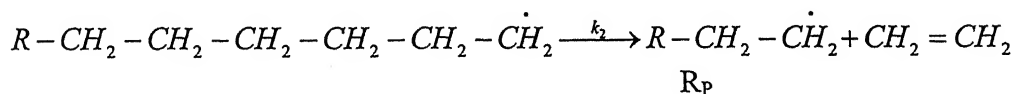
Free Radical Mechanism:

All pyrolysis reactions of organic materials occur mostly by free radical mechanism and this can also be used to explain depolymerization in the presence of catalysts. The general reaction conditions for free radical behaviour are high temperature and relatively non-polar liquid phase media. The depolymerization mechanism is assumed to be same as that for polymerization and includes initiation, depropagation, hydrogen abstraction and termination steps. Bockhorn et al. ²⁴ has proposed free radical mechanism for thermal degradation of polyethylene where in the initiation occurs by random scission of the polymer chain into primary radicals denoted by R_p . The β scission of these radicals leads to the formation of ethane followed by intramolecular hydrogen transfer and this leads to a more stable secondary radicals R_s . Subsequent β scission of the secondary radicals contributes to the radical chain mechanism as there is a primary radical being formed in each step and the termination occurs by the combination of two primary radicals. This mechanism is given below:

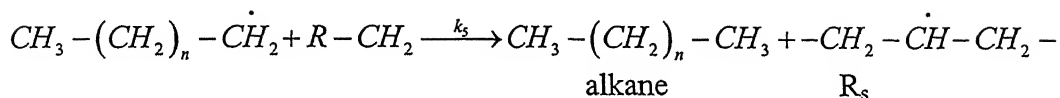
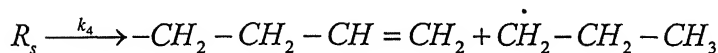
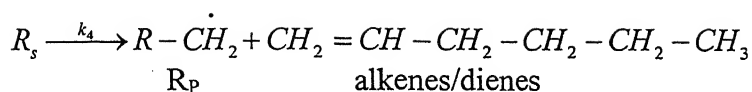
Initiation



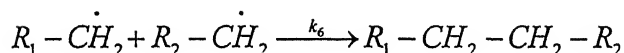
Propagation



β-Scission



Termination

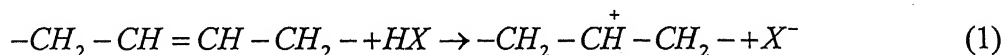


Carbonium ion Mechanism:

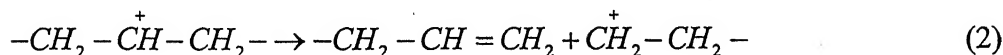
The catalytic effects of solid acid catalyst in degradation of plastics are due to their acidic properties ^{25,26}. Buekens et al. ²⁷ has proposed a mechanism for polyethylene degradation.

Initiation

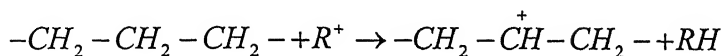
Initiation may occur on some defect sites of the polymer chain, an olefin linkage could be converted into an on-chain carbonium ion by proton additon as



Then the polymer chain may be broken up through the β-scission as follows



Initiation may also take place through random hydride ion abstraction through by low molecular weight carbonium ions (R^+).



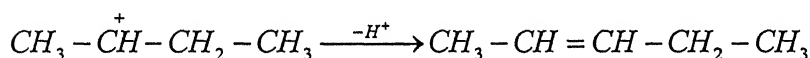
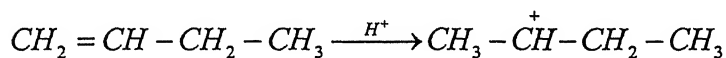
This carbonium ion then undergoes the β -scission as in equation 2.

Depropagation

The molecular weight of the main polymer chain is reduced through successive attacks by acid sites or other carboniumions. The chain cleavage occurs leading to the formation of an oligomer fraction ($\sim C_{30} - C_{80}$). This undergoes further cleavage probably by direct β -scission of chain end carbonium ions which leads to the formation of gases and a liquid fraction ($C_{10} - C_{25}$).

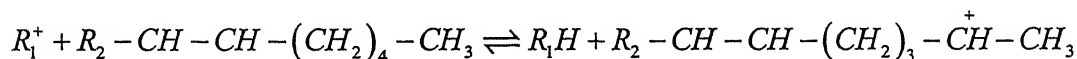
Isomerization

The carboniumion intermediates undergo rearrangement by hydrogen or carbon atom shifts.

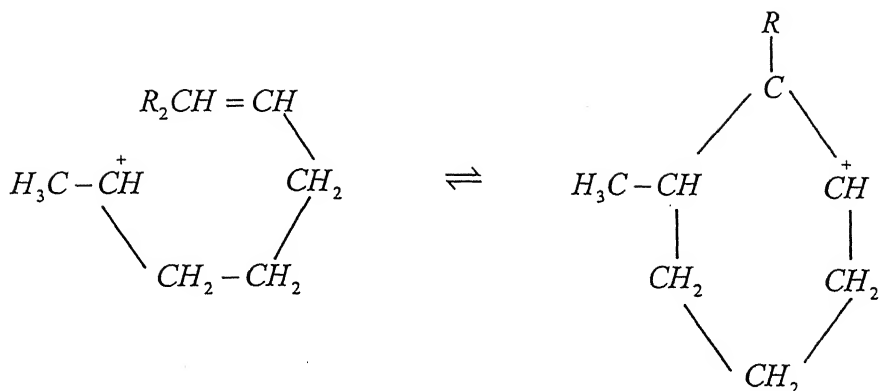


Aromatization

Some carbonium ion intermediates undergoes cyclization reactions.



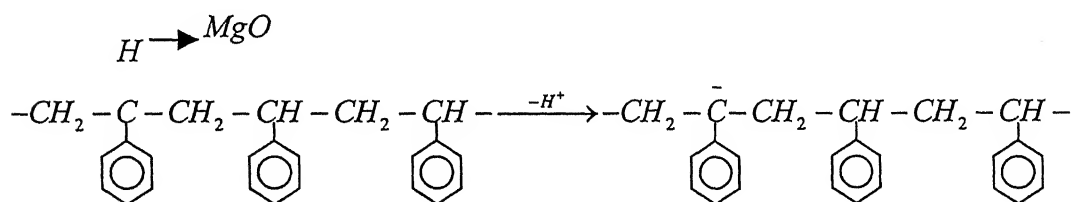
This carbonium ion undergoes intramolecular attack on the double bond.



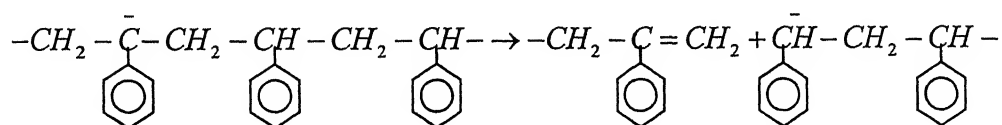
Carbanion Mechanism:

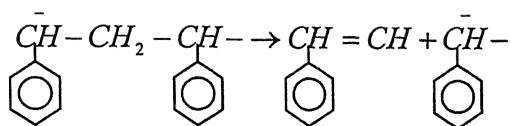
The degradation of polymers in presence of base catalysts is assumed to proceed through the formation of carbon anions and this mechanism includes initiation, depropagation, hydrogen abstraction and termination steps. Zhang et al. proposed a mechanism for depolymerization of polystyrene in presence of base catalysts in which a proton attached to a backbone tertiary carbon is removed by the base catalyst. As a result of this rate of initiation increases and thus rate of depolymerization also increases. The mechanism is given below.

Initiation:

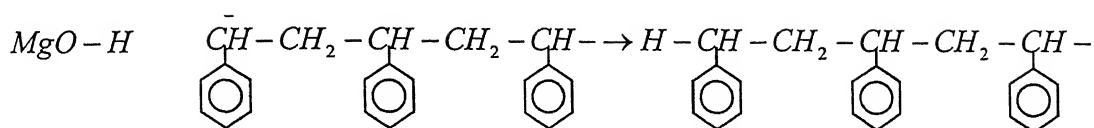


Depropagation:





Termination:



Selective and partial oxidation of hydrocarbons to oxygen containing compounds (alcohols, aldehydes, ketones and acids) is extremely important and useful for the chemical industry. Terminally oxidized hydrocarbons serve as potential feedstock for the chemical pharmaceutical industry. However these reactions represent a challenge because more than one oxygenated product is invariably produced from a given starting material. In addition all products are susceptible to complete combustion to CO_2 . From mechanistic considerations, oxidation reactions can be divided into three categories.

1. Auto oxidation via free radical chain reaction
2. Oxidation of the substrate coordinated to the metal ion followed by reoxidation of the reduced metal.
3. Catalytic oxygen transfer.

The dominance of one of the reactions depends on the reaction condition (gas or liquid phase, reaction temperature and pressure), the nature of the metal and the oxidizing agent.

The oxidation of cyclohexane is an important reaction from the industrial point of view that it can be oxidized to adipic acid. The other oxidation products mainly formed are cyclohexanol and cyclohexanone and these can be further oxidized to adipic acid and caprolactum. Luna et al.²⁸ studied the oxidation of cyclohexane in presence of transition metal incorporated on aluminophosphate catalysts. In presence of vanadium and chromium metal salts the principal products formed was cyclohexanone with cyclohexanol and cyclohexene in minor amounts. The yield of cyclohexanone in presence of vanadium and chromium metal salts were 72% and 54% respectively. Rabion et al.²⁹ studied the oxidation of cyclohexane in an aqueous micelle system with t-butylhydroperoxide in presence of biomimetic methane monooxygenase enzyme complexes. The major products formed were cyclohexanone and cyclohexanol.

Patron et al.³⁰ studied the oxidation of cyclohexane catalyzed by iron-phthalocyanine complexes encapsulated in Y- zeolite with tertiary butylhydroperoxide as oxidant. The products formed were cyclohexanone and cyclohexanol with high selectivities for cyclohexanone (95%) and conversion of 25%. Yamanaka et al.³¹ studied the partial oxidation of cyclohexane by using SmCl_2 dissolved in a mixed solvent of CH_3COOH , CH_2Cl_2 and H_2O in the presence of zinc powder at ambient conditions. The conversion of the reaction varied from 2 to 30% for different concentrations of SmCl_2 . Cyclohexanone and cyclohexanol were formed and the selectivity of cyclohexanone was 54%. Stykove et al.³² studied the oxidation of cyclohexane with air in presence of mesoporous molecular sieves of the type MCM-41. The products formed were cyclohexene, cyclohexanol and cyclohexene-2-one. Talsi et al.³³ studied the role of alkylperoxo complexes of cobalt (III) in catalytic oxidation of cyclohexane by cumene

hydroperoxide in the presence of bis(acetylacetonato) cobalt (II). The yield of cyclohexanol and cyclohexanone was 15% and 10% respectively.

Perkas et al.³⁴ studied the oxidation of cyclohexane in presence of isobutyraldehyde as an activator catalyzed by nano structured iron and cobalt oxides and iron supported on titania under mild conditions (atmospheric pressure). When nano structured amorphous iron oxide was as catalyst the conversion was very low while under the same operating conditions when sonochemically prepared iron oxide was used as catalyst the conversion was higher (~10%) with around 90% selectivity for the target products of cyclohexanol and cyclohexanone. Ling et al.³⁵ studied the liquid phase oxidation of cyclohexane, using cyclohexanone as a coreactant, glacial acetic acid as a solvent and CoAPO-5 as the catalyst. The products formed were adipic acid, glutaric acid and succinic acid, the yield of adipic acid being 65% at 30% conversion of cyclohexane at 135°C. It was observed that the synergism effect of cyclohexane and cyclohexanone could result in a decrease in the apparent activation for cyclohexane oxidation and propionic acid results in the highest reaction rate when the temperature is below 135°C. Kulakarni et al.³⁶ studied the oxidation of cyclohexane in presence of polymer support with schiff base functional group with cobaltous palmitate as the catalyst. The conversion of cyclohexane was 20.48% at temperature of 150°C 5.44 atm pressure and the products formed were cyclohexanol (11.82%) and cyclohexanone (8.66%).

Pires et al.³⁷ studied the liquid phase oxidation of cyclohexane with tert-butylhydroperoxide in presence of rare earth exchanged zeolite Y as catalyst. At 90°C the conversion of cyclohexane was 10% and the yields of cyclohexene, n-hexanal, cyclohexanone and cyclohexanol were 6.82%, 1.08%, 1.98%, 2.86% respectively.

However at this temperature carboxylic acid was formed due to overoxidation of n-hexanal. Sooknoi et al.³⁸ studied the oxidation of cyclohexane in presence of titanium containing zeolite catalysts and acetic acid was used as solvent. Cyclohexanone was obtained as the product and it was found that in presence of acetic acid there was an increase in activity.

Very little information is available in case of catalytic oxidation of n-heptane. In absence of catalyst, oxidation occurs at higher temperatures with low selectivity. Dagaut et al.³⁹ studied the oxidation of n-heptane in a jet stirred reactor from low to high temperature (550-1150°K) and pressure (1-40 atm). The products formed were methanol, methane, ethene, ethylene, acetylene, acetaldehyde, ethylene oxide, propane, propene, butene, 1-pentene, 1-hexene, 1-heptene and many other unidentifiable compounds. It was observed that the conversion was low in lower temperature range. Minetti et al.⁴⁰ studied the oxidation of n-heptane in a rapid compression machine at low and intermediate temperatures and high pressures. Eight C₇ heterocycles, lower 1-alkanes, heptenes, aldehydes and carbon monoxide were obtained as products. Stoylkova et al.⁴¹ studied the partial oxidation of n-heptane at 523°K in presence of SAPO-5, SAPO-11, BEA and MCM-41 molecular sieves. The product formed was a mixture of heterocyclic compounds (2-methyl-5-ethyl-furan and 2,6-dimethyl-pyran), heptanones, 4-methyl-1,4-hexadiene and 2,4-dimethyl-1,3-pentadiene. Small amount of 1-hepten-4-ol was also formed.

Catalytic reforming is an important reaction for upgrading the octane number of gasoline without changing the carbon number constituents. It allows in transforming n-paraffins of low octane number (ON), especially with five or six carbon atoms, into isoparaffins and dehydrocyclized products of high octane numbers. From a thermodynamic

point of view, the formation of high octane dibranched isomers is favored at low temperature and the best isomerization catalysts are strong acidic materials which work at the lowest possible temperatures.

The following two types of catalysts have generally been used in industrial processes ⁴².

1. Platinum on chlorinated alumina, which is very active at low temperature (150⁰C).

However it is very sensitive to poisoning by water, oxygen, organic nitrogen and sulphur. In addition, the process requires a continuous addition of chloride precursor to the feed, which represents a major drawback.

2. Platinum on mordenite is less active than the platinum on alumina due to the lower acid strength and hence operated at a higher temperature (250⁰C). However, unlike platinum on chlorinated alumina, they are resistant to poisoning.

Guevara et al. ⁴³ studied the isomerization of n-hexane on sulfated mixed oxide of alumina-zirconia catalysts with the different composition of Al₂O₃-ZrO₂. At 250⁰C and 1 atm the conversion of n-hexane was 18.5% and the C₆ isomers formed were 2,2-dimethylbutane, 2,3-dimethylbutane and 2-methylpentane with a selectivity of 8%, 34% and 54% respectively. Buchholz et al. ⁴⁴ studied the transformation of n-hexane in the temperature range 150-320⁰C in the presence of Pt/sulfated zirconia catalyst and found that methylpentanes were formed with high selectivities (80-100%) which decreased with increasing temperature. Pierre et al. ⁴⁵ studied the isomerization of n-hexane in presence of molybdenum oxide catalyst in the temperature range 300-400⁰C. In the beginning, isomerization was dominant reaction, however with increasing time, cracking of alkanes is found to be more predominant. It was also observed that at higher reaction temperatures cracking occurred more quickly. Matsushashi et al. ⁴⁶ studied the isomerization of n-butane

and n-pentane in presence of solid super acids of sulfated zirconia and platinum promoted sulfated zirconia. In case of skeletal isomerization of n-butane, a long induction period was observed for catalytic activity and product composition. Only iso-butane was formed during the induction period and both butane and iso-butane were converted into propane and pentane after that time. In case of n-pentane, with the addition of n-butane or iso-butane, iso-pentane was formed and for this mixture as the feed no induction period was observed. Boskovic et al.⁴⁷ studied the isomerization of n-hexane over catalyst having (0.5 wt%) Pt deposited on Na(H)Y in the temperature range 200-350°C. It was found that optimum selectivity with the maximum isomer yield was obtained for the catalyst as acid sites of required strength and well dispersed metal sites were generated simultaneously through an optimal metal-support interaction. Patrylak et al.⁴⁸ studied the isomerization of n-hexane over natural zeolites containing palladium catalysts in the temperature range 250-300°C. The conversion was found to increase with increasing reaction temperature and the maximum conversion obtained was 79.5%.

Hashimoto et al.⁴⁹ studied the effect of acidic and basic properties on selectivity in the reforming of n-hexane over a binary oxide of titanium and zirconium supporting a platinum catalyst, which has both acidic and basic sites. The rates of formation of cyclic and aromatic products increased linearly with the number of adjacent pairs of acid-base sites. The reaction rates for cracking and isomerization were proportional to the number of lone acid sites. Ali et al.⁵⁰ studied the hydroisomerization, hydrocracking and dehydrocyclization of n-pentane and n-hexane in the temperature range 300-500°C using mono and bimetallic catalyst promoted with fluorine. The study reveals that hydroisomerization produced isoalkanes, hydrocracking produced methane, ethane and

propane and dehydrocyclization produced methylcyclopentane and benzene. The reaction temperature influenced both acidity and selectivity while incorporation of the second metal and fluorination improved the acidity of Pt/Al₂O₃ catalyst. Gallo et al.⁵¹ studied the isomerization of n-heptane in presence of SiC supported MoO₃ – carbon- modified catalyst. The products obtained were dimethylpentanes, 2-methylhexane, 3-methylhexane and 3-methylpentane. Falco et al.⁵¹ studied the effect of platinum concentration on tungsten oxide promoted zirconia over the catalytic activity for n-hexane isomerization. It was found that the catalyst activity and stability increases for platinum concentration above 0.05% because of higher hydrogen availability at surface. Further increments in platinum concentration do not produce important modifications in catalytic activity or hydrogen availability. Beltramini et al.⁵² studied the catalytic reforming of n-heptane on platinum, tin and platinum-tin supported on alumina at 500°C and 5 bar. The use of the bimetallic catalyst results in the control of coke deposition, increase stability and improve aromatics yield. Isomerization reactions were significant in presence of Pt/Al₂O₃ and Sn/Al₂O₃ catalyst while dehydrocyclization reactions were significant in presence of Pt-Sn/Al₂O₃, low in presence of Sn/Al₂O₃ and passed through a maximum on Pt/Al₂O₃. Toluene was the main product over all catalyst. Leu et al.⁵³ studied the isomerization of n-hexane in presence of platinum loaded zeolite β and it was found to be highly selective for dimethylbutane.

The main objectives of this thesis are:

1. Synthesize catalyst for depolymerization of HDPE and reforming and functionalization of alkanes. For this purpose, the zirconium complex was molecularly bound on modified carbamated alumina and modified carbamated silica gel supports. The alumina supported zirconium complex catalyst catalyzed depolymerization of HDPE while functionalization and reforming of alkanes were catalyzed by silica gel supported zirconium complex catalyst.
2. Characterize the synthesized modified carbamated supports and the final catalysts.
3. Identify the products formed on reforming of n-hexane, oxidation of n-heptane and cyclohexane and depolymerization of HDPE.
4. Study the effect of reaction time and reaction temperature on the conversion and the product distribution during the reforming and oxidation reactions.

Chapter 2

Experimental Details

2.1 Catalyst Preparation

In this work the zirconium complex was loaded on modified carbamated alumina and modified carbamated silica.

2.1.1 Synthesis of benzoyl isocyanate

Benzoyl isocyanate was prepared by the reaction of sodium azide (35g, 0.538gmole) with equal number of moles of benzoyl chloride in presence of dry benzene (20ml). The reaction was carried out at 0°C for 8 hours, after which it was filtered. The permeate was benzoyl isocyanate formed according to the reaction.



The product thus prepared had a matching IR from literature.

2.1.2 Synthesis of 1,2 bis-(salicylidine amino)-phenylene

The o-phenylenediamine (10.8g, 0.1gmole) is reacted with salicylaldehyde (24.4g, 0.2gmole) by condensation reaction in absolute ethanol (25ml) to give the complex. The reaction mixture was stirred for 3 hours, after which the yellow precipitate appears. It was filtered, and then dried. The dried material thus obtained was 1,2 bis-salicylidine amino-phenylene.

2.1.3 Synthesis of zirconium complex

The 1,2bis-(salicylidine amino)-phenylene (1.5g) was dissolved in acetonitrile (100ml) and heated till 65°C. Zirconium oxychloride (10g) was dissolved in distilled water (200ml) and then mixed with 1,2 bis-(salicylidine amino)-phenylene solution. The reaction mixture was kept for 30 minutes after which a yellow coloured precipitate was formed. This precipitate was separated, washed with acetonitrile and then dried at 80°C. The dried material thus obtained was zirconium complex.

2.1.4 Synthesis of molecularly bound zirconium complex on modified carbamated alumina support

2.1.4a Reaction of benzoyl Isocyanate with alumina

Alumina pellets (20g) were taken in a round bottom flask and to this, the prepared benzoyl isocyanate was added. This was allowed to react for 24 hours. The pellets obtained after the reaction were washed with dry benzene, then dried in an oven at 80°C. The hydroxyl group present on the surface of alumina⁵⁹ react with benzoyl isocyanate to form carbamated alumina.

2.1.4b Synthesis of alumina supported zirconium complex catalyst

The carbamated alumina pellets were refluxed for 8 hours at 80°C with dichloroethane (50ml) in presence of lewis acid catalyst. The chloride group reacted with carbamate as well as the with the phenyl group on alumina. The zirconium complex was dissolved in acetonitrile and then added to the modified carbamated alumina pellets. This

was then refluxed for 8 hours at 80°C after which the pellets were washed with acetonitrile and dried. The pellets turned yellow indicating metal loading.

2.1.5 Synthesis of molecularly bound zirconium complex on modified carbamated silica gel support

2.1.5a Synthesis of hydroxylated silica gel

Silica gel (40 g) was washed with distilled water followed by acetone washing and then dried in oven at 80°C. The dried material was added to 100 ml of HCl (35% by weight) and refluxed for 4 hours at 50°C. After this, the silica gel was filtered and washed with distilled water and acetone again. It was dried in an oven at 80°C. The dried material thus obtained was hydroxylated silica gel.

2.1.5b Reaction of benzoyl isocyanate with hydroxylated silica gel

Hydroxylated silica gel (40g) was taken in a round bottom flask to which benzoyl isocyanate (120ml) was added. The mixture was stirred at 40°C for 6-8 hours. Then it was filtered and the material obtained on filter paper was washed with dry benzene, then dried. The dry material thus obtained was carbamated silica gel.

2.1.5c Synthesis of silica gel supported zirconium complex catalyst

The carbamated silica gel (40g) is refluxed for 8 hours at 80°C with dichloroethane (50 ml) in presence of ZnCl_2 (5 mg) which remains in the reacting broth. The chloride group reacted with carbamate as well as with the phenyl group on silica gel. The zirconium complex was dissolved in acetonitrile and then added to modified carbamated silica gel. This was then refluxed for 8 hours after which the silica gel was

was washed with acetonitrile and then dried at 80°C. The silica gel turned yellow indicating the metal loading.

2.2 Depolymerization of HDPE

2.2.1 Experimental setup

The setup used for HDPE degradation is shown in fig. 2.2. Experiments were conducted in a high pressure batch reactor (C) made of stainless steel with a volume of 100 ml. The reactor has a pressure indicator (B) and a provision for gas inlet. The reactor was heated to the desired temperature by placing it in a furnace (D). High temperature up to 900°C can be achieved with this furnace. A temperature controller (A) was used to control the temperature and a thermocouple (E) was inserted into the reactor for sensing the temperature.

2.2.2 Experimental procedure for depolymerization

Experiments were conducted under batch operation in presence of the modified carbamated alumina supported zirconium complex catalyst. For each run the feed consisted of 20 grams of HDPE and 2 grams of the catalyst. After charging the reactor with the feed the air in the reactor was purged out using nitrogen gas, then closed with a zero pressure gauge value. The reactor was then placed in the furnace and heated to the desired temperature for the desired time. On cooling, the reactor was depressurized, the products were taken out and then analyzed using GC and GCMS analysis. The GC column used was

ULBON HR-1, fused silica capillary of 50 m length and GCMS data were obtained on a Shimadzu QP- 2000 instrument at 250⁰C. GC was used to determine the number of compounds present in the product mixture and the individual compounds were identified using mass spectra obtained from GCMS analysis.

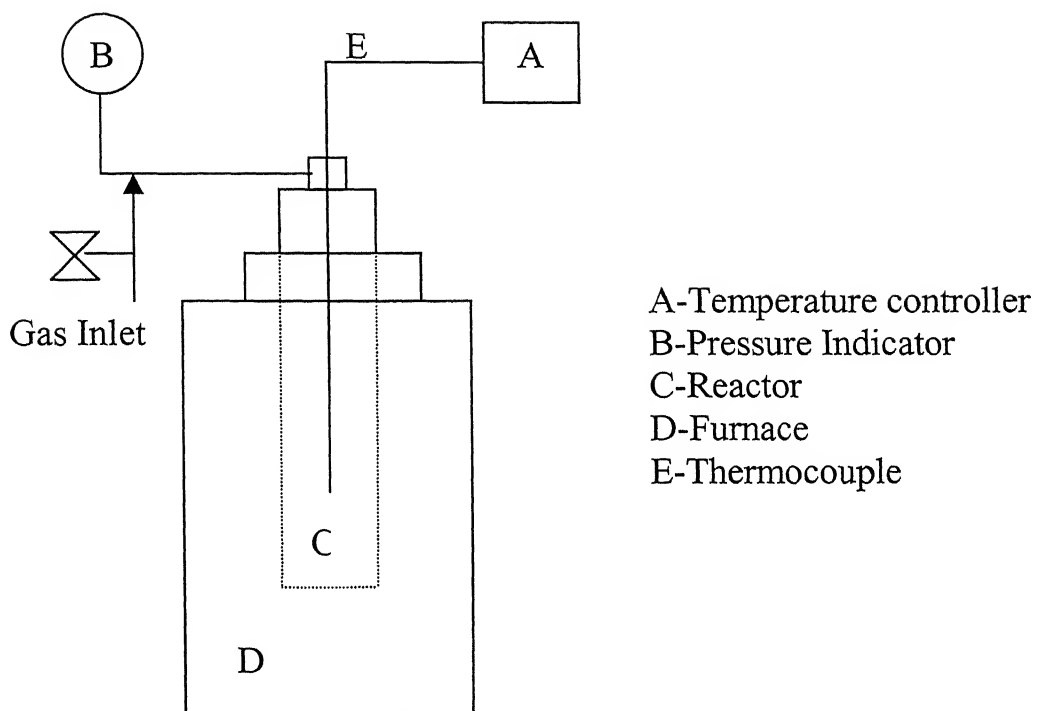


Figure 2.2 Schematic diagram of the experimental setup for depolymerization

2.3 Reforming and Oxidation of Alkanes

2.3.1 Experimental setup

Experiments have been conducted in a rocking type-high pressure batch reactor setup shown in fig. 2.3. The reactor is made of stainless steel (volume 380ml) and was heated by external electrical coil. An on/off controller controlled the temperature with a thermocouple for temperature sensing. The reactor has pressure indicator and provision for gas inlet.

2.3.2 Experimental procedure

Reforming of n-hexane in nitrogen environment and oxidation of n-heptane and cyclohexane using molecular oxygen was studied under batch operation in presence of silica gel supported zirconium complex catalyst. For each run, the reaction feed consisted of reactant (100ml) and catalyst (0.5grams in case of n-hexane and n-heptane and 1 gram in case of cyclohexane). After applying the initial gas pressure (100psi), the reactor was heated to the desired temperature and the reaction was run for the desired time. The product was taken out and then it was analyzed by gas chromatography (GC) and gas chromatography mass spectroscopy (GCMS) analysis. The GC column used was ULBON HR-1, fused silica capillary of 50 m length and GCMS data were obtained on a Shimadzu QP- 2000 instrument at 250°C. GC was used to determine the number of compounds present in the product mixture and the individual compounds were identified using mass spectra obtained from GCMS analysis.

TC- Temperature Controller

PG- Pressure Gauge

TE- Thermocouple

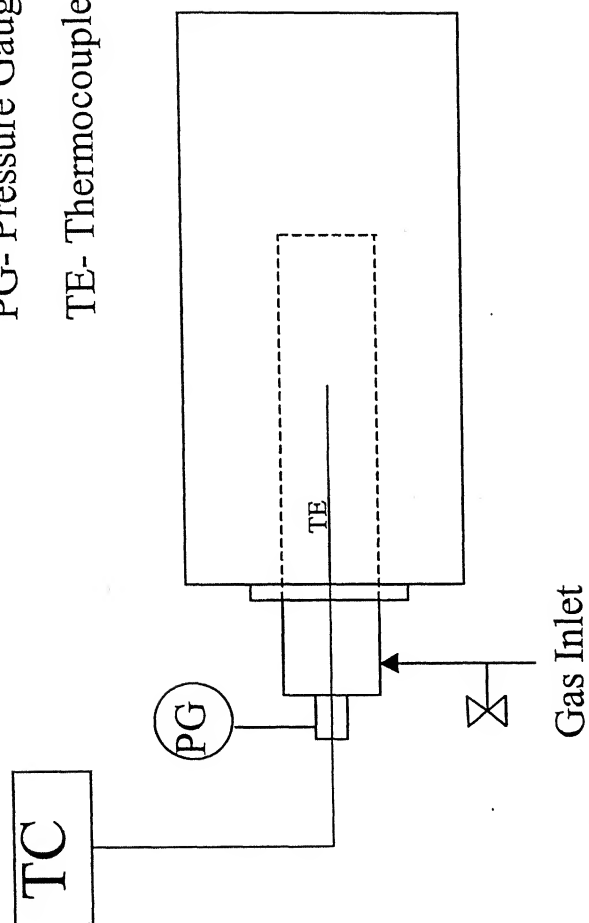


Figure 2.3 Schematic diagram of the experimental setup for reforming and oxidation

2.4 Calculations

2.4.1 Calculation of Conversion

The percentage conversion of reactant is calculated as

$$\%Conversion = \left(1 - \frac{\text{number of moles of the reactant at the end of the reaction}}{\text{number of moles of the reactant at } t=0}\right) * 100$$

2.4.2 Calculation of Yield

The yield of a particular product is given by

$$\%Yield = \frac{\text{number of moles of particular product at the end of the reaction}}{\text{total number of moles of the reactant at } t=0} * 100$$

2.4.3 Calculation of Selectivity

The selectivity of a particular product is given by

$$\%Selectivity = \frac{\text{number of moles of a particular product at the end of the reaction}}{\text{total number of moles of the reactant reacted at the end of the reaction}} * 100$$

Chapter 3

Catalyst Characterization

Fourier Transform Infrared (FT-IR) Analysis

3.1 Characterization of modified carbamated silica gel

supported zirconium complex catalyst

Hydroxylated silica gel was prepared and the presence of hydroxyl group was confirmed by its FT-IR (-OH at 3448 cm^{-1}) given in fig. 3.1.1. Benzoyl isocyanate was synthesized and its FT-IR (aromatic -CH at 3038 cm^{-1} and N-C=O at 2351 cm^{-1}) is given in fig. 3.1.2 and matched with literature. The carbamate group was bound on the silica gel by reacting hydroxylated silica gel with benzoyl isocyanate. The carbamate group on the silica gel was confirmed by its FT-IR (aromatic -CH at 3038 cm^{-1} , -NH group at 1598 cm^{-1} , C=O at 1693 cm^{-1}) fig. 3.1.3. 1,4-bis(salicylidene amino)-phenylene (used in the preparation of zirconium complex) was prepared by the reaction of o-phenyldiamine and salicylaldehyde. Its FT-IR is given in fig. 3.1.4 and it was matched with that given in the literature. The carbamate group bound silica gel was reacted with dichloroethane in presence of lewis acid for further modification. The FT-IR (Si-O at 801 cm^{-1} , N-C=O at 2356 cm^{-1} and C-Cl at 693 cm^{-1}) of the silica gel obtained after this step is given in fig. 3.1.5. The FT-IR (aromatic -CH at 3038 cm^{-1} , Si-O at 801 cm^{-1} , -OH at 3437 cm^{-1} , C=O at 1635 cm^{-1}) of the final modified carbamated silica gel supported zirconium complex catalyst is given in fig. 3.1.6.

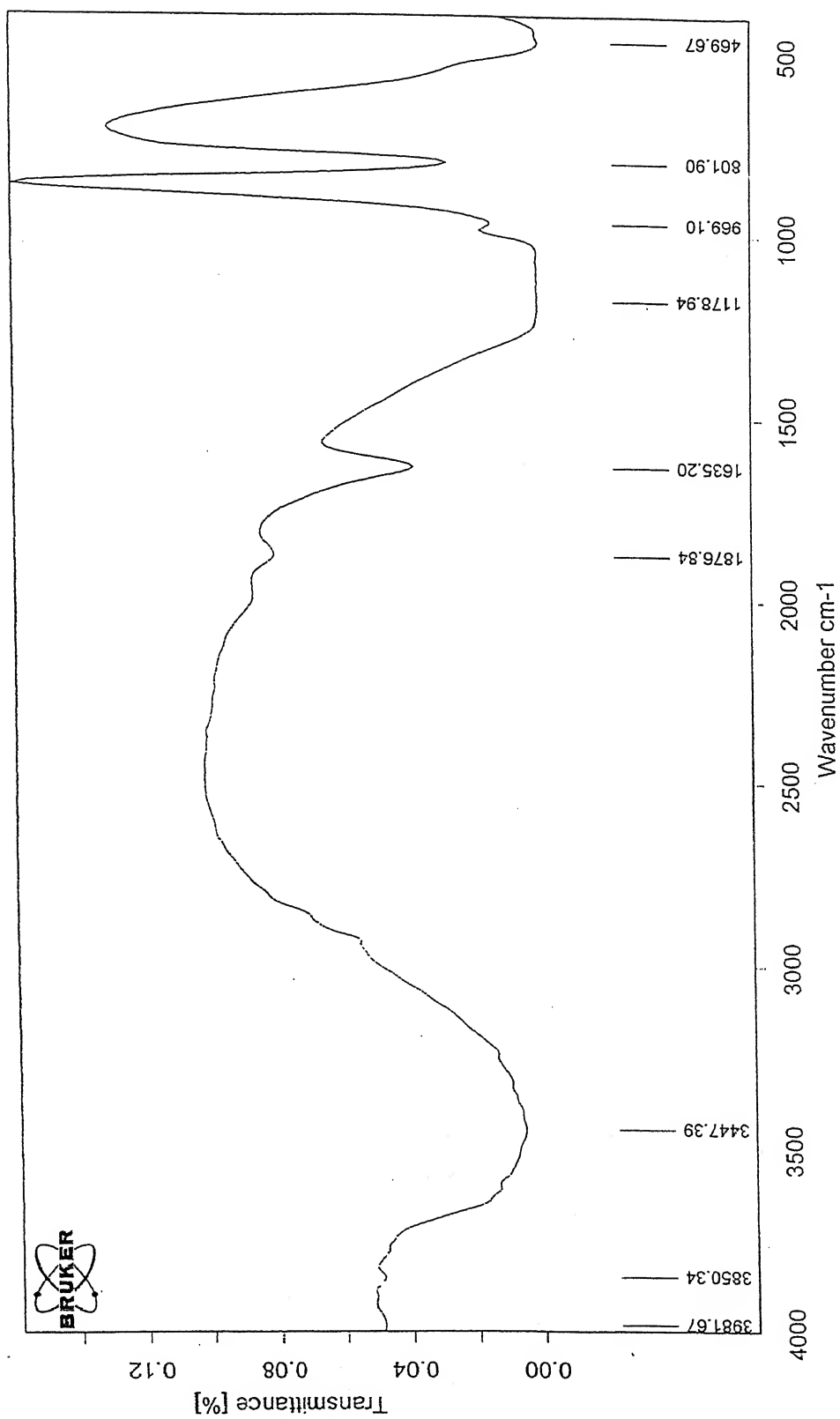


Figure 3.1.1 FT-IR spectra of hydroxylated silica gel

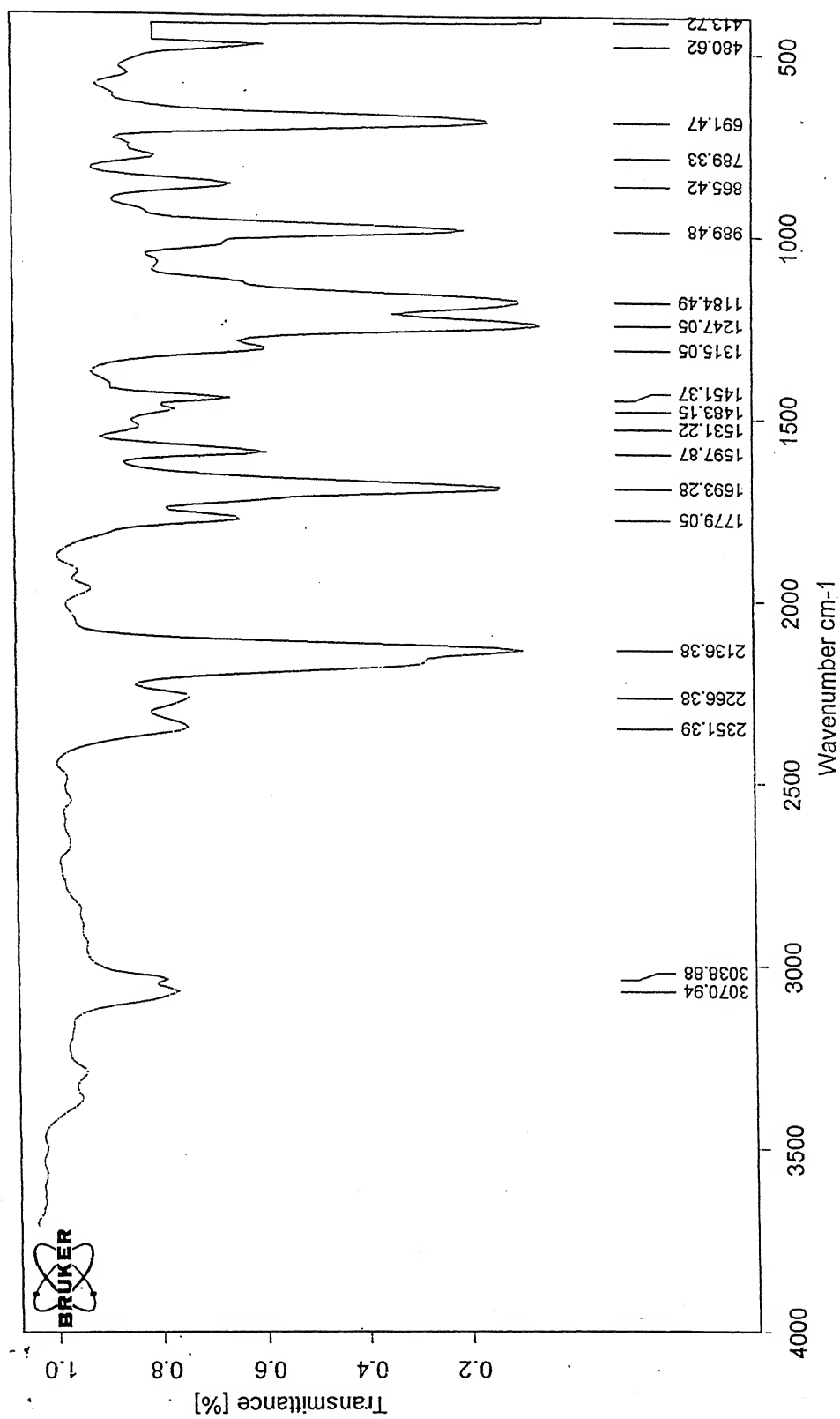


Figure 3.1.2 FT-IR spectra of benzoyl isocyanate

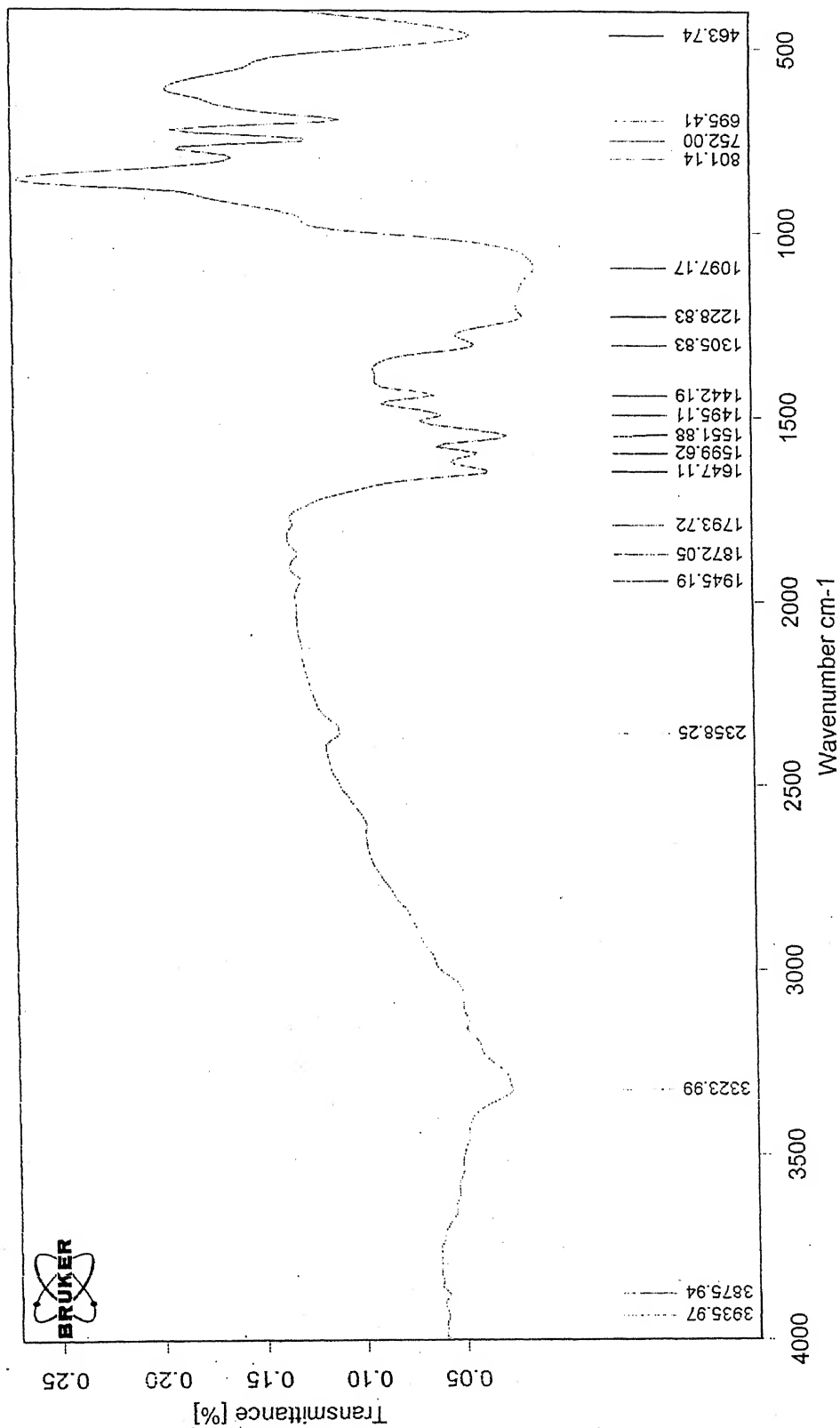


Figure 3.1.3 FT-IR spectra of carbonate group bound on silica gel

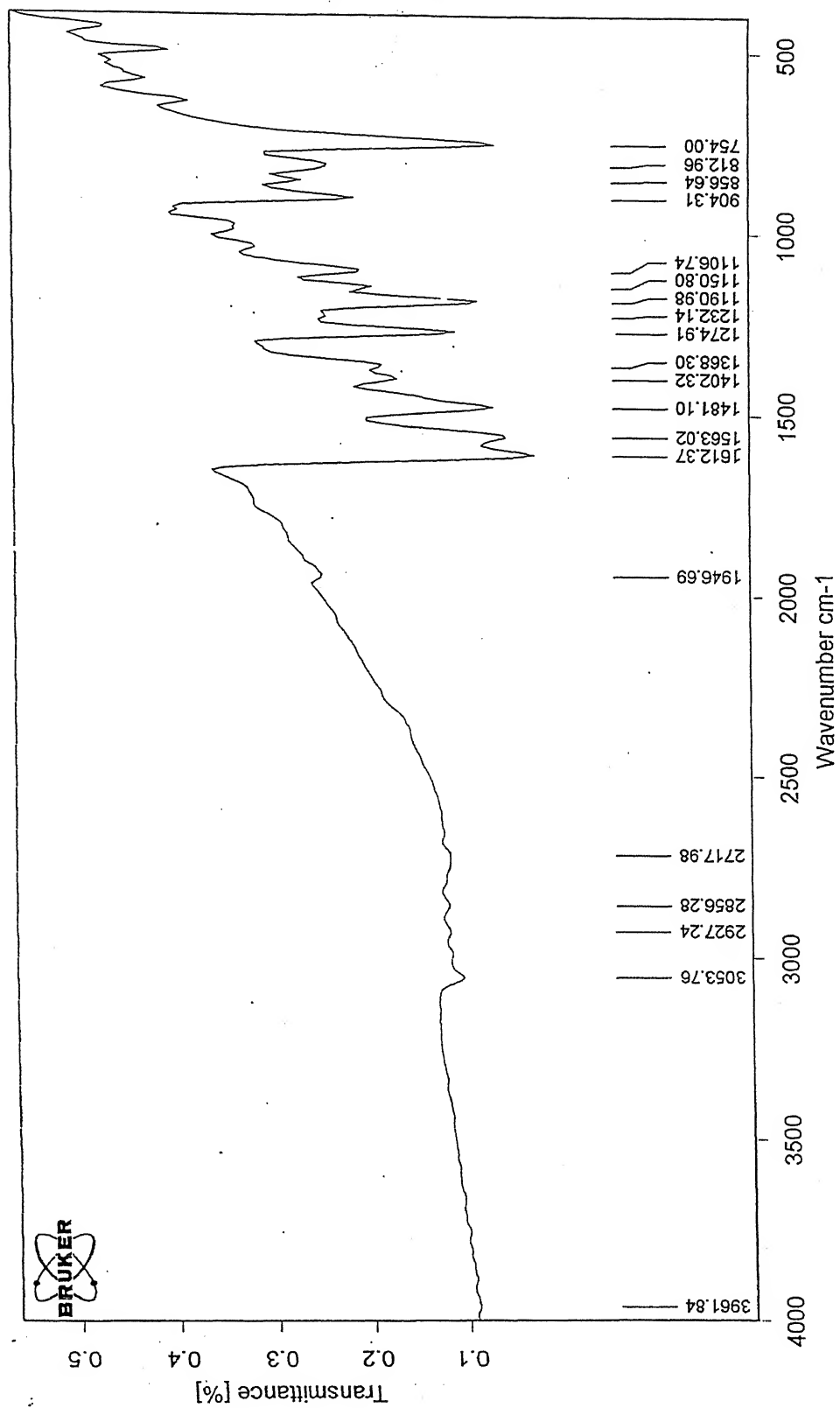


Figure 3.1.4 FT-IR spectra of 1,4-bis(salicylidene amino)-phenylene

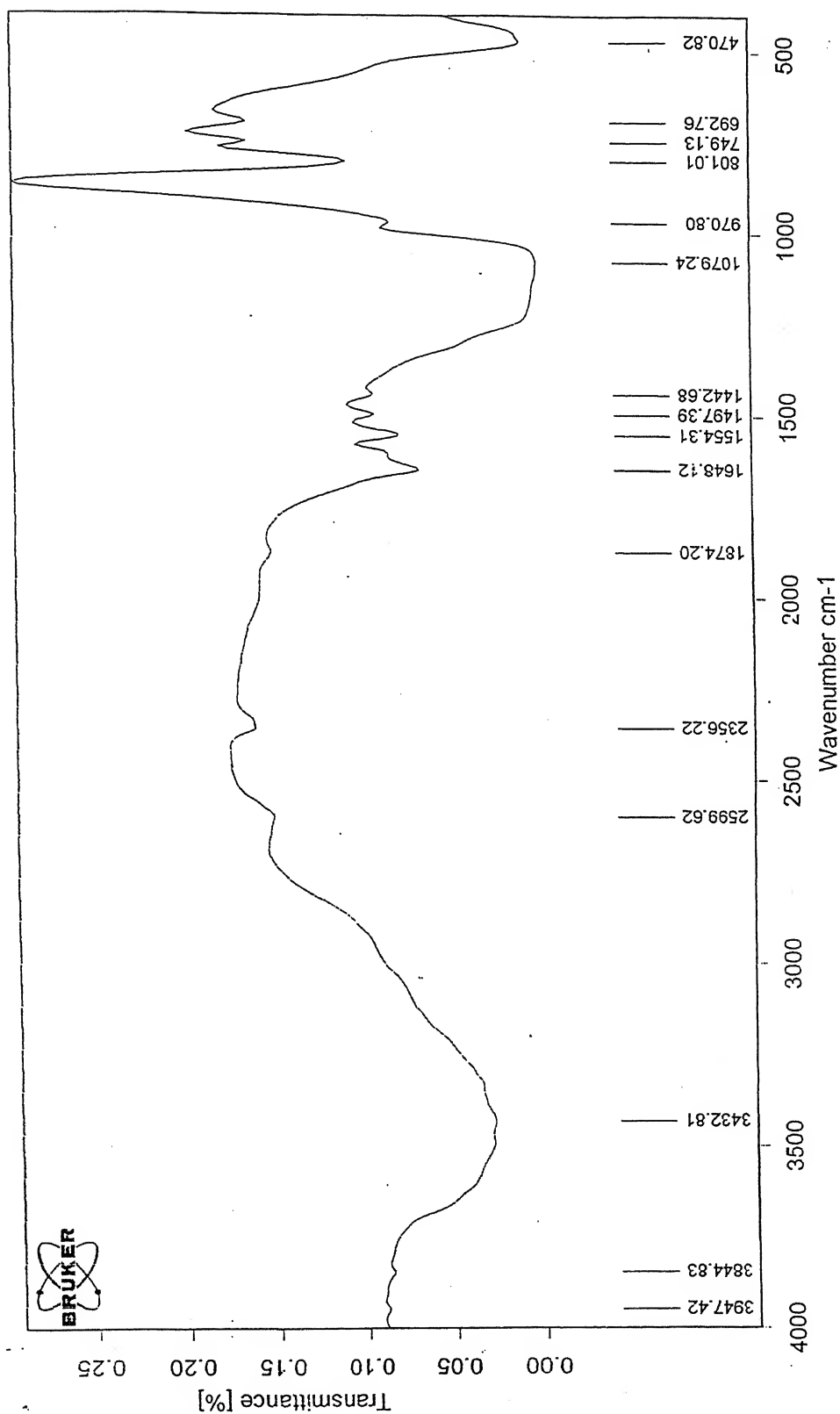


Figure 3.1.5 FT-IR spectra of the compound formed by the reaction of carbamate group bound on silica gel with dichloroethane

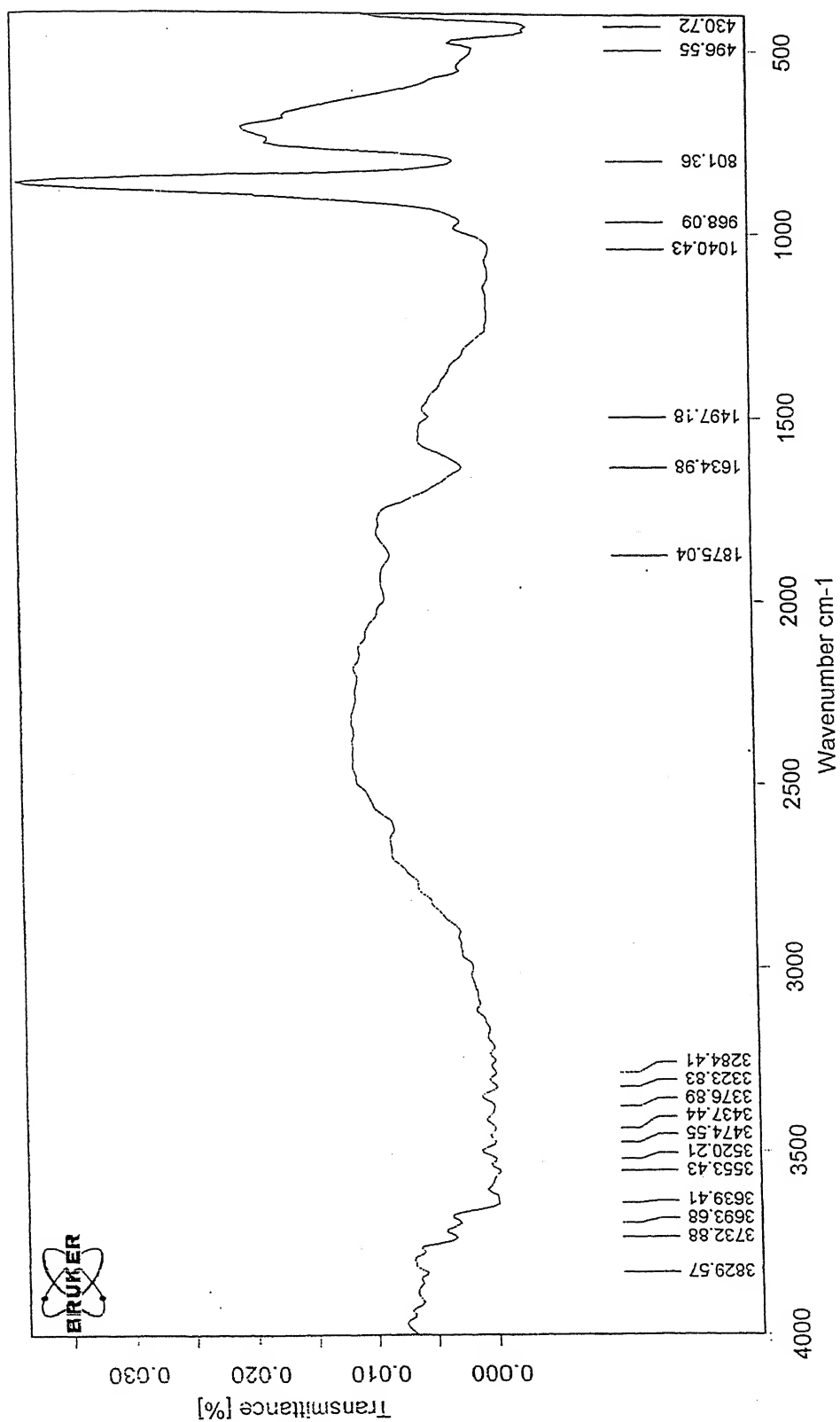


Figure 3.1.6 FT-IR spectra of silica gel supported zirconium complex catalyst

3.2 Characterization of modified carbamated alumina .

supported zirconium complex catalyst

The presence of hydroxyl group on the surface of alumina ⁵⁹ is shown in its FT-IR (-OH group at 3452 cm^{-1}) and it is given in fig. 3.2.1. The carbamate group was bound on alumina by the reaction of hydroxyl group present on the alumina surface and benzoyl isocyanate and the carbamate group on alumina was confirmed by its FT-IR (aromatic -CH at 3044 cm^{-1} , C=O at 1654 cm^{-1}) given in fig3.2.2. The carbamate group bound alumina was reacted with dichloroethane in presence of lewis acid. The FTIR (aromatic -CH at 3042 cm^{-1} , C-Cl at 633 cm^{-1}) of alumina obtained after this step is given in fig 3.2.3. The FT-IR (aromatic -CH at 3042 cm^{-1} , -OH group at 3452 cm^{-1}) of the final modified carbamated alumina supported zirconium complex catalyst is given in fig 3.2.4.

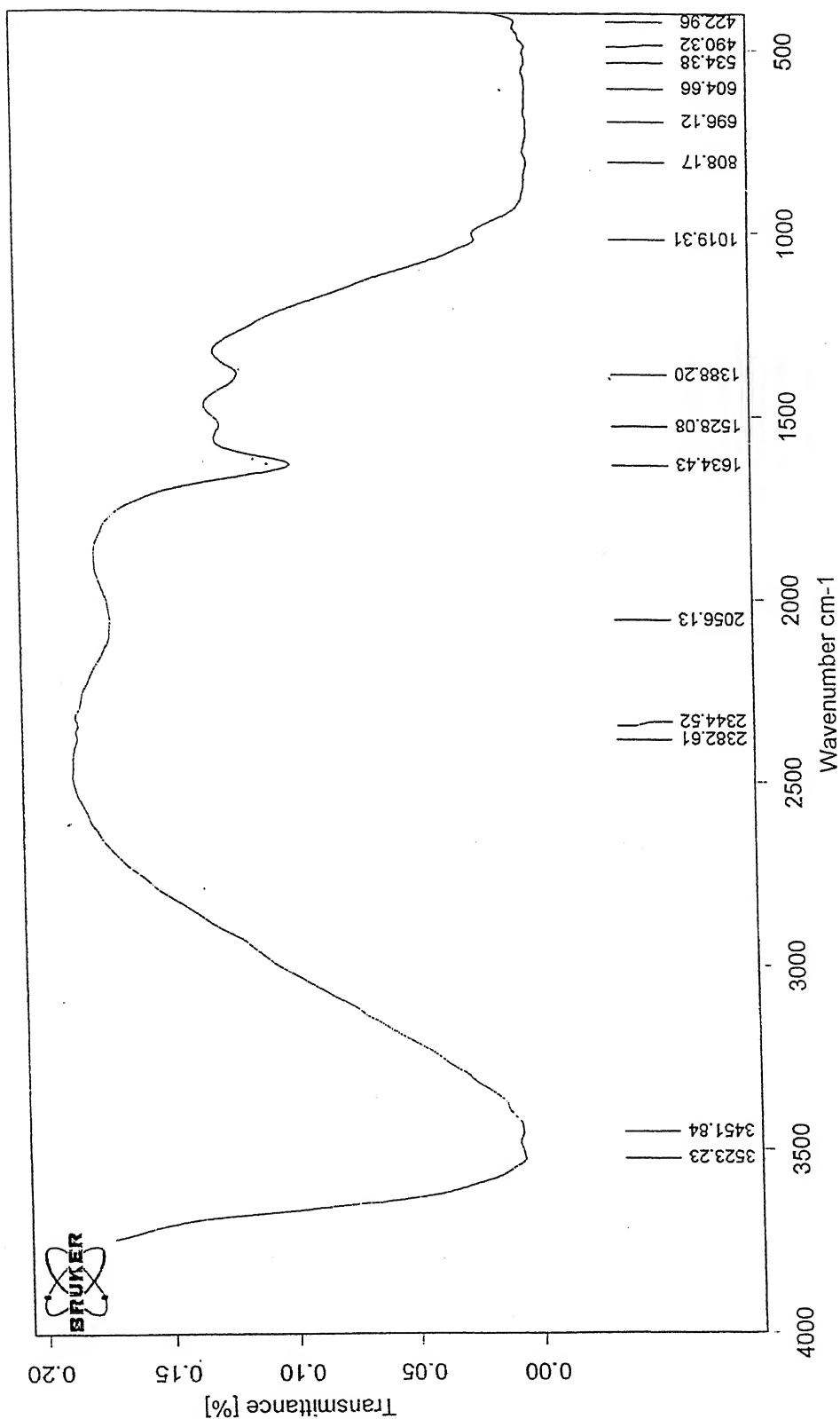


Figure 3.2.1 FT-IR spectra of alumina

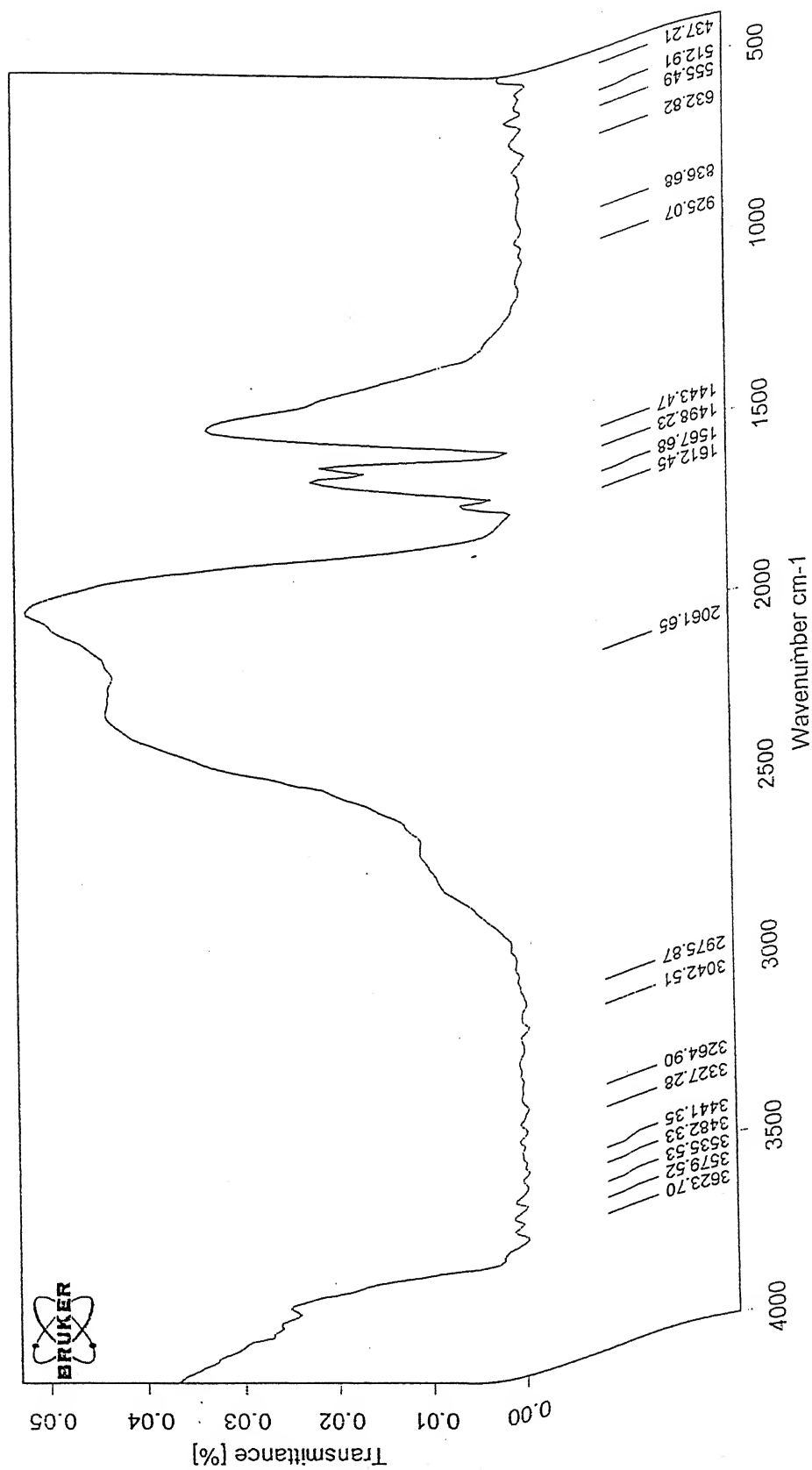


Figure 3.2.3 FT-IR spectra of the compound formed by the reaction of carbamate group bound on alumina with dichloroethane

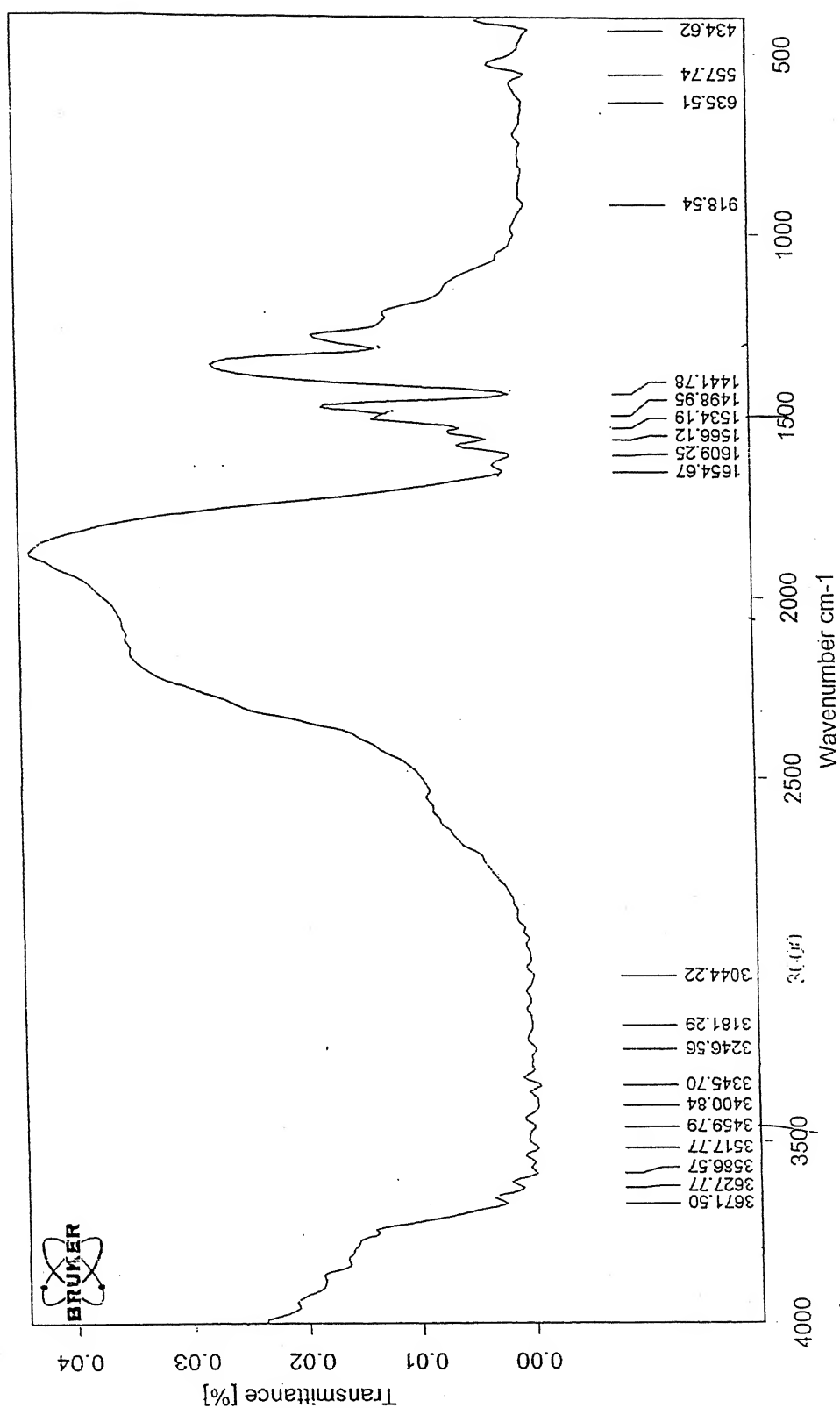


Figure 3.2.2 FT-IR spectra of carbamate group bound on alumina

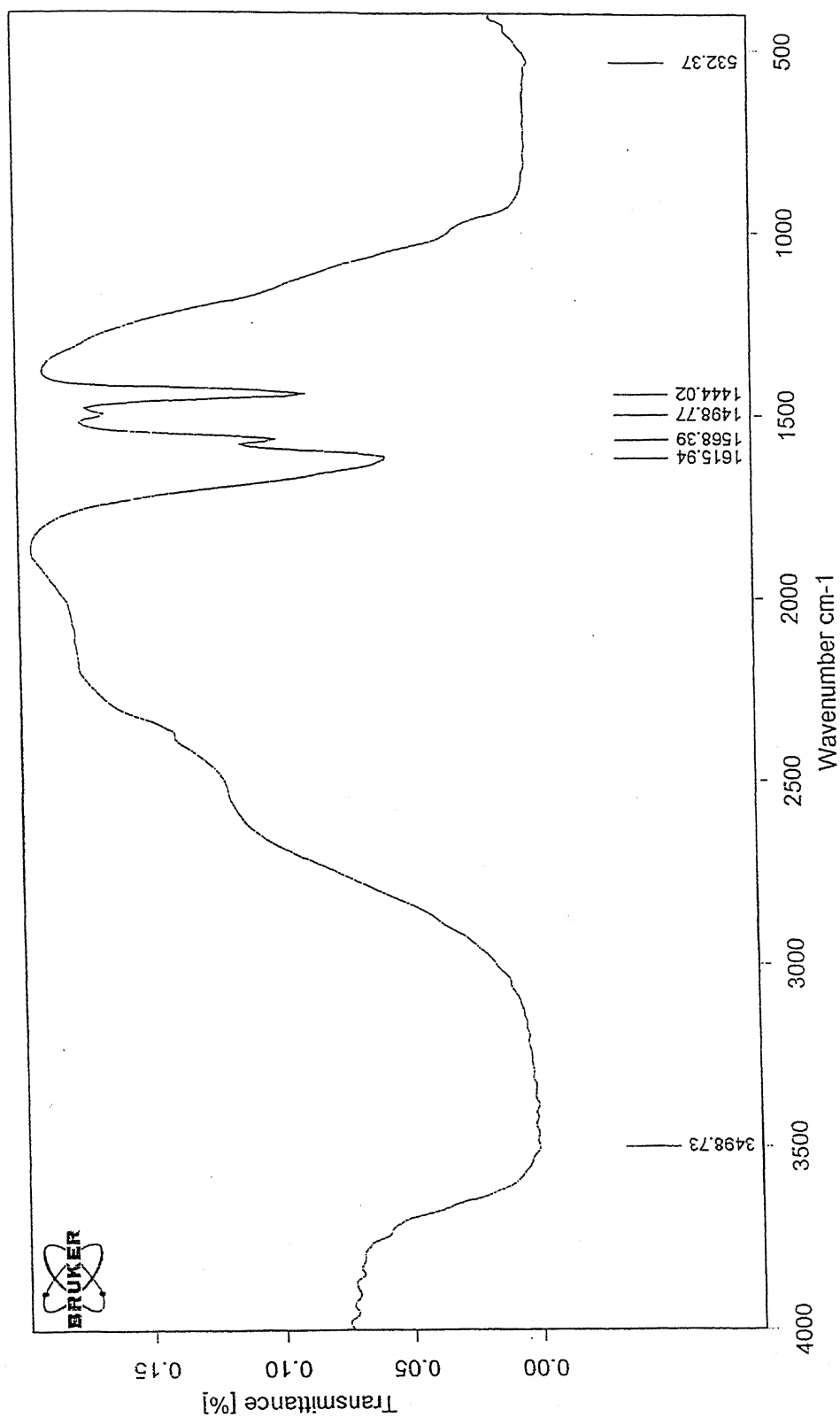


Figure 3.2.4 FT-IR spectra of alumina supported zirconium complex catalyst

Chapter 4

Results and Discussion

4.1 Reforming of n-hexane in presence of molecular nitrogen

The reforming of n-hexane was studied in batch reactor keeping the mass of the catalyst (0.5 g) constant at different temperatures (between 120⁰C and 190⁰C) and for different reaction period (from 2 hours to 12 hours) in nitrogen environment. For the product of one of the runs (at 190⁰C temperature, 100 psig initial nitrogen pressure and 8 hours reaction time), fig. 4.1 shows the gas chromatograph (GC) which gives a total of 5 major peaks. The identification of these compounds has been done by the mass spectra of the compounds corresponding to the peaks in the GC and these spectra were matched with those given in the literature. Peak-1 has been identified as 2-methylpentane (2-MP), peak-2 as 3-methylpentane (3-MP), peak-3 as hexane (H), peak-4 as methylcyclopentane (MCP) and peak-5 as cyclohexane (CH) and the mass spectra of these compounds are given in appendix (A1). It can be seen that both isomerization products (2-MP and 3-MP) and dehydrocyclization products were formed for all reaction periods and at all reaction temperatures. The commercial catalytic reforming reactions generally occur at high temperatures (350⁰C – 500⁰C) and takes place in hydrogen environment ⁵⁵. The overall reaction consists of four competing reactions viz. cracking, isomerization, dehydrocyclization and aromatization reactions. One of the commercially used reforming catalyst is platinum supported on alumina (Pt/Al₂O₃) and reforming of n-hexane in presence of this catalyst forms isomerization products (2-MP, 3-MP, 2,2-DMB and 2,3-DMB), cracking products (C₁–C₅), dehydrocyclization product (MCP) and aromatization

product (benzene). Bimetallic catalysts are also being used in which the second metal (Re, Rh, Ir, Sn) is incorporated into $\text{Pt/Al}_2\text{O}_3$ and this catalyst shows an improvement in hydroconversion activity and selectivity⁵⁰. In some cases, the acidity of the support is increased by chlorination and fluorination and this leads to a higher hydro conversion. The support has a considerable influence on the overall mechanism, for example, by replacement of Al_2O_3 by Na(H)Y zeolite, the catalyst shows higher selectivity for isomerization products and operates in the temperature range of 200°C - 350°C ⁴⁷. When a binary oxide of titanium and zirconium (having both acid and base site) was used, as support there is a profound effect on the specificity of the various reaction products formed⁴⁹. Instead of platinum, palladium has been supported on natural zeolite and this catalyst operates in the temperature range of 200°C - 350°C ⁴⁸. HMCM-22 catalyst (having no metal operating in the temperature range of 240°C – 370°C) has been used for n-hexane isomerization⁴² and is found to give cracking products in larger amounts. The supported zirconium complex catalyst reported in this work operates in mild conditions i.e. in presence of nitrogen (100psig) at temperatures as low as 120°C and there is no formation of 2,2-DMB, 2,3-DMB, alkenes, benzene or cracked products demonstrating the specificity of the catalyst.

The conversion and product distribution as a function of reaction time was studied for a reaction period of 2 to 12 hours at a fixed temperature of 160°C and the initial nitrogen pressure was kept 100 psig. Fig. 4.1.1 shows the variation of conversion with reaction time and it appears that it has almost reached a steady value of around 71.5% in the time interval under study. The variation of yield and selectivity with reaction time is

shown in fig. 4.1.2 and 4.1.3 respectively. For 8 hours reaction time the yield of 2-MP, 3-MP, MCP and CH were 26.24%, 21.86%, 20.46% and 3.986% respectively.

The effect of temperature on the conversion as well as the product distribution was studied in the temperature range of 120⁰C-190⁰C keeping the initial nitrogen pressure (100psig) and reaction time (8 hours) constant. As seen from fig. 4.1.4 there is no commendable change in conversion with increase in reaction temperature and it is around 72% in the temperature range under study. The variation of yield and selectivity with temperature is shown in fig. 4.1.5 and 4.1.6 respectively. It appears that only in the case of cyclohexane there is a slight decrease in yield with increase in temperature in the range 140⁰C – 190⁰C while for the rest of the compounds there is no significant change in yield. The yield of 2-MP, 3-MP and MCP were around 25.5%, 21.5% and 20.5% respectively. The yield of cyclohexane was 3.99% at 140⁰C and this was the highest in the temperature range under study. At 190⁰C the amount of unidentified products increases and so there is a possibility of cracking reactions occurring at and beyond 190⁰C. At all temperatures the yield of the isomerization products exceeds the yield of the dehydrocyclized products.

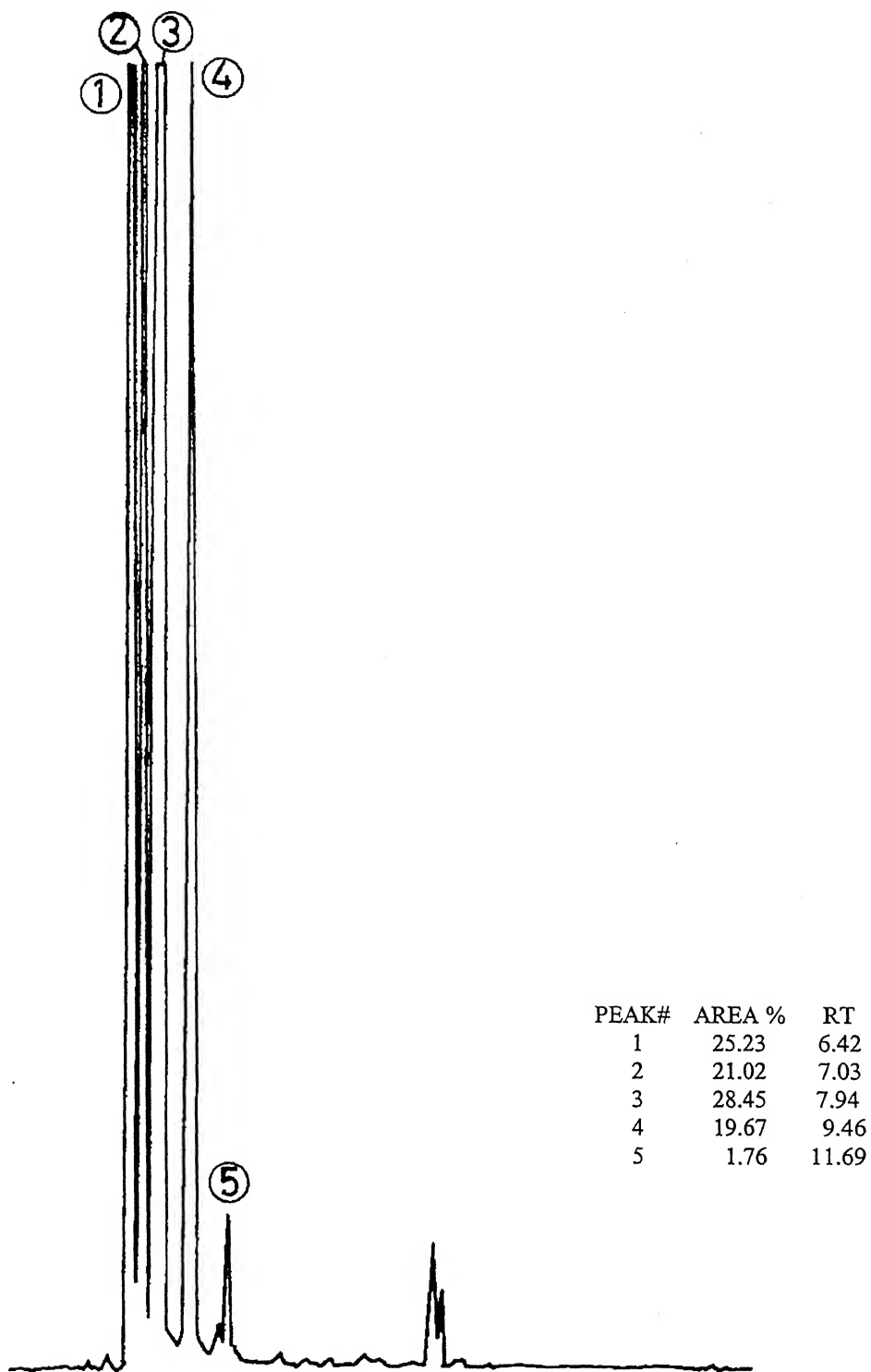


Figure 4.1 Gas chromatograph of the product formed on reforming of n-hexane

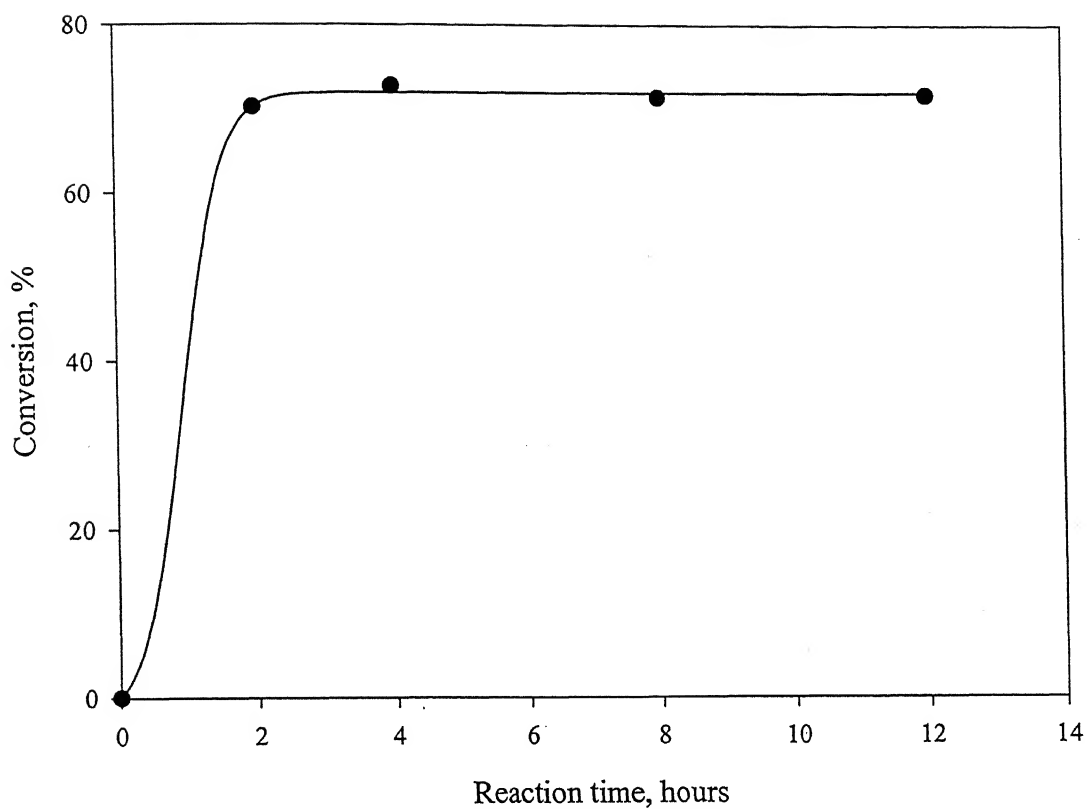


Figure 4.1.1 Effect of reaction time on the overall conversion of n-hexane

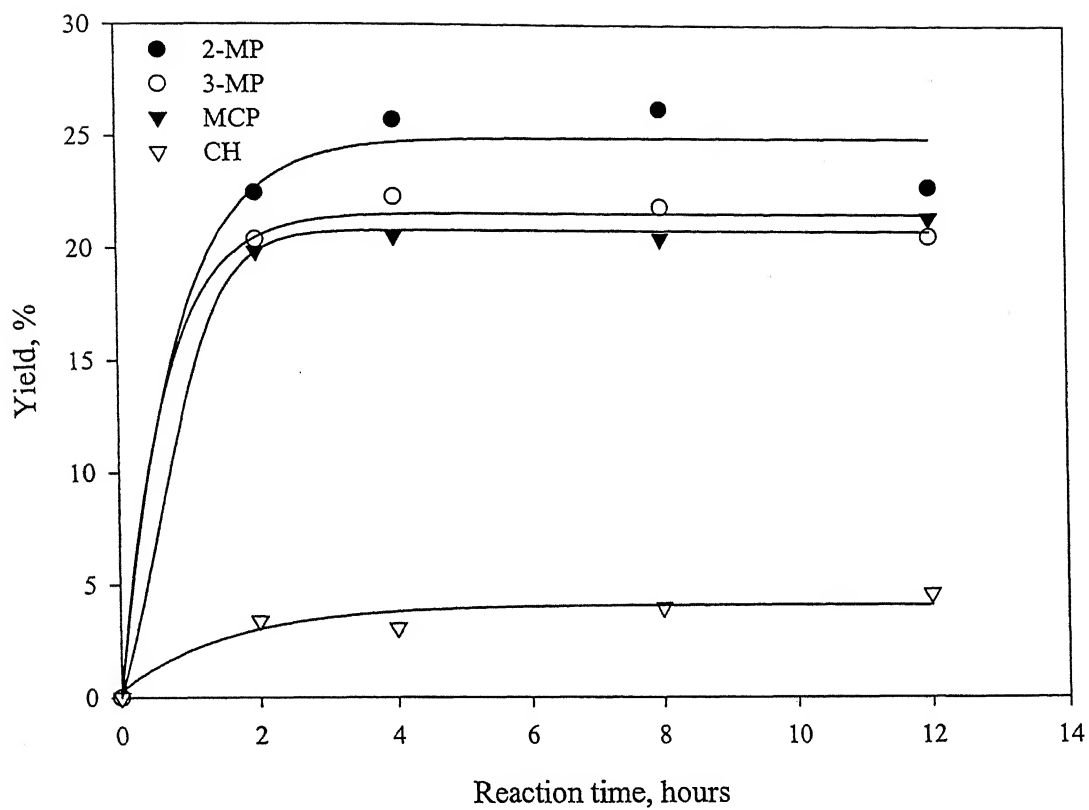


Figure 4.1.2 Effect of reaction time on the yield of the products formed on catalytic reforming of n-hexane

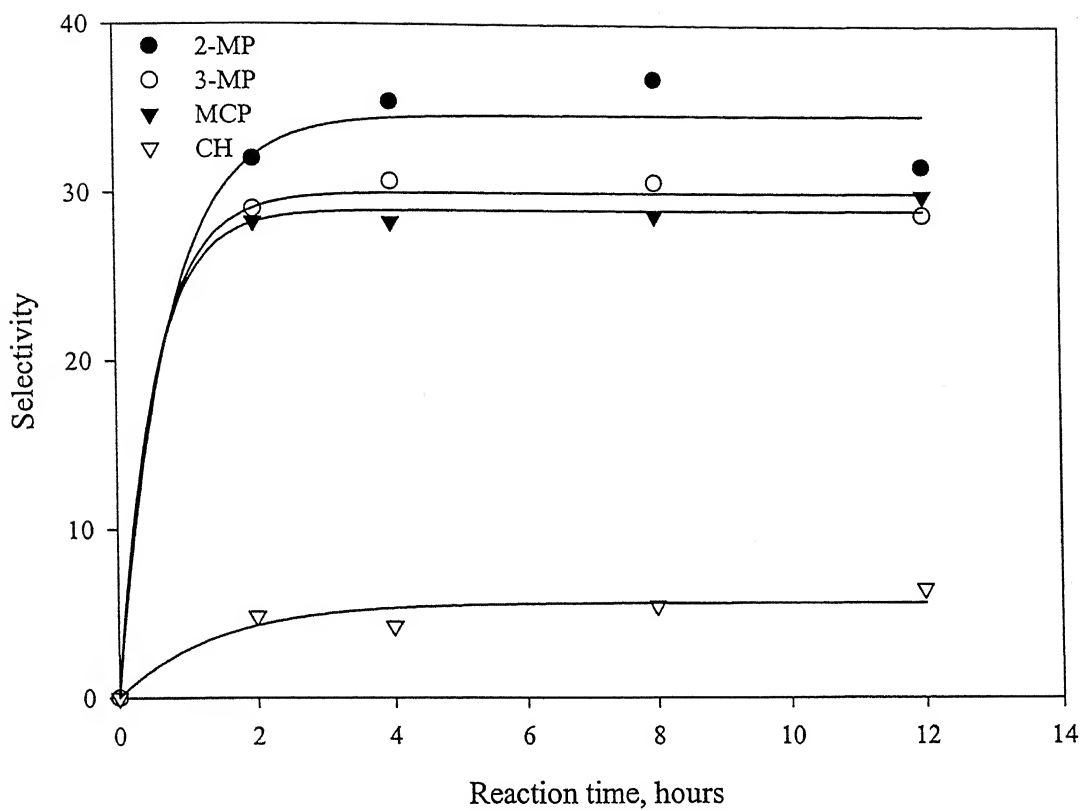


Figure 4.1.3 Effect of reaction time on the selectivity of the products formed on catalytic reforming of n-hexane

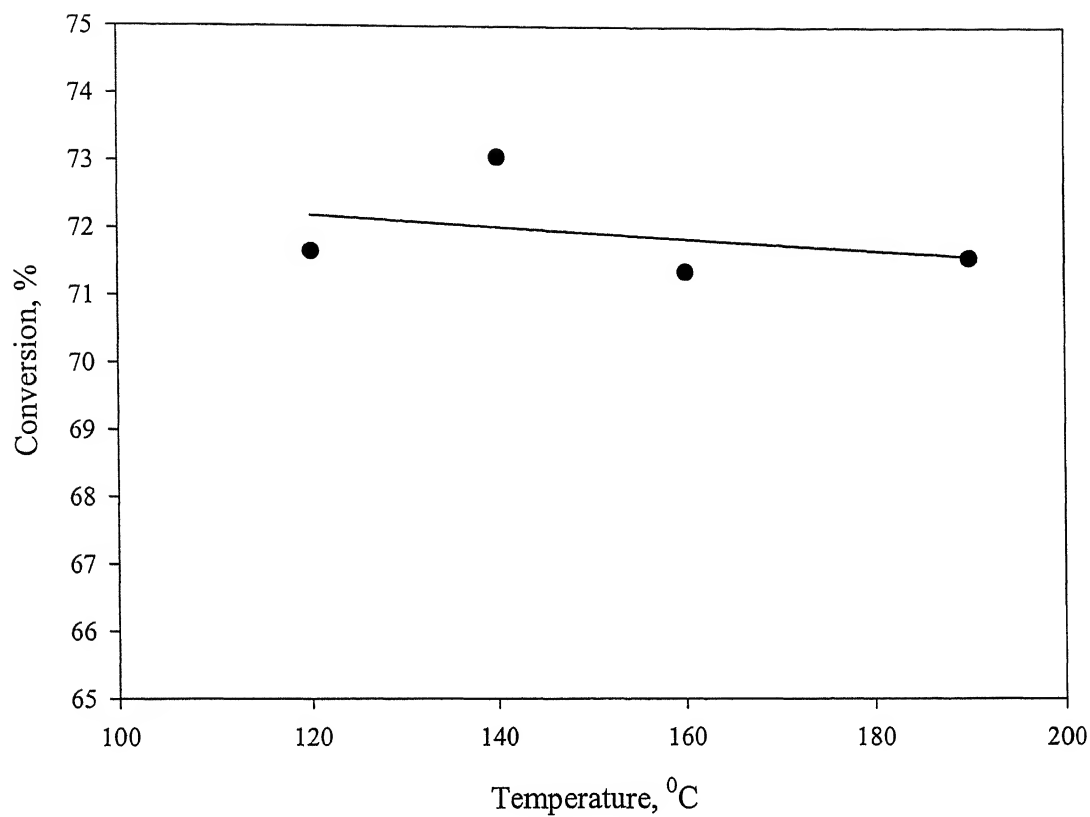


Figure 4.1.4 Effect of reaction temperature on the overall conversion of n-hexane

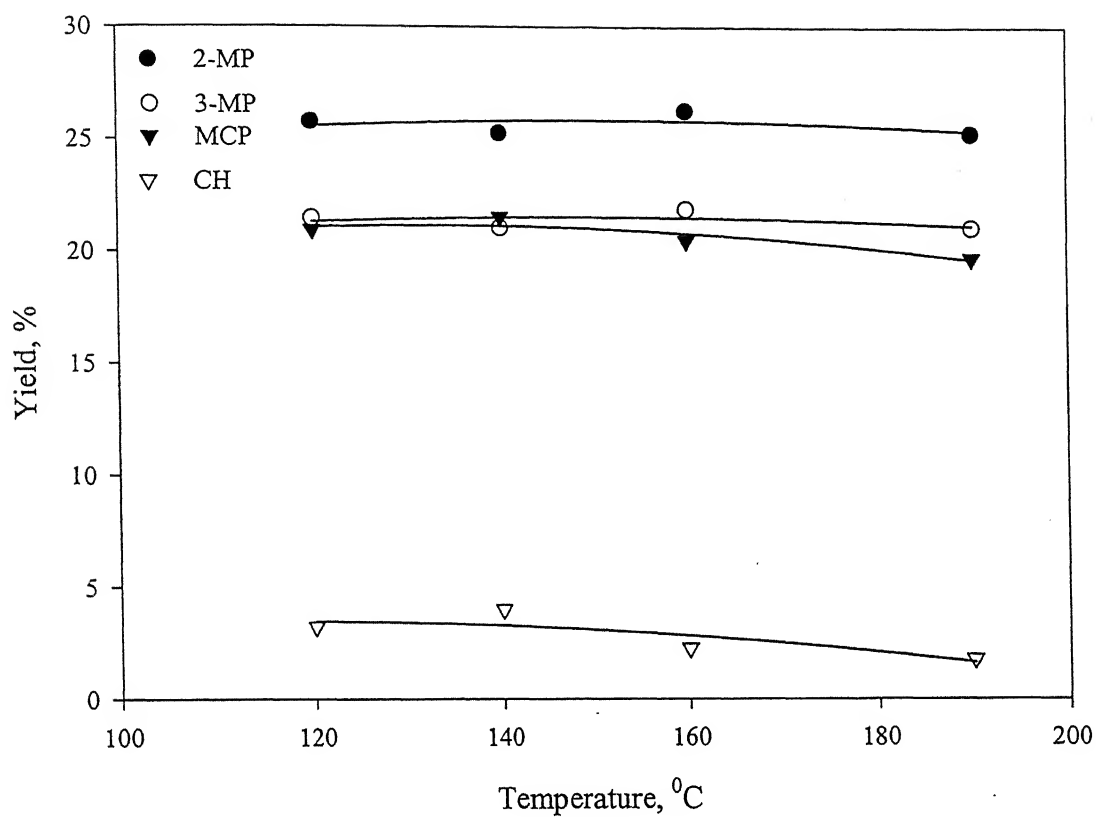


Figure 4.1.5 Effect of reaction temperature on the yield of the products formed on catalytic reforming of n-hexane

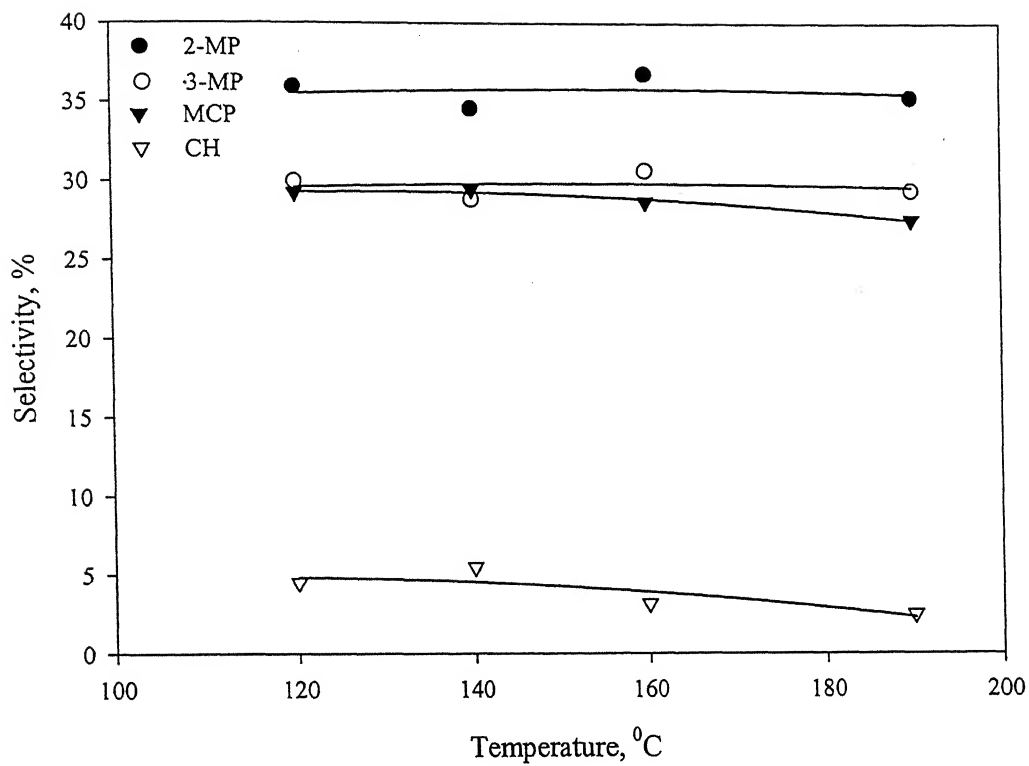


Figure 4.1.6 Effect of reaction temperature on the selectivity of the products formed on catalytic reforming of n-hexane

4.2 Oxidation of n-heptane in presence of molecular oxygen

The oxidation of n-heptane has been studied in a batch reactor keeping the mass of the catalyst constant (0.5g) at different temperatures (between 160°C and 220°C) and for different reaction period (between 2 to 12 hours). For the product of one of the runs (at 200°C temperature and 8 hours of reaction time), fig. 4.2 shows the gas chromatograph and is found to show a total of six major peaks. The identification of these compounds has been done by mass spectra of the compounds corresponding to the peaks in the GC and matching them with those given in literature. Peak-1 has been identified as 2-methylpentane (2MP), peak-2 as methylcyclopentane (MCP), peak-3 as 4-methyl,1-pentene (4-M1-Ptene), peak-4 as heptane (H), peak-5 as cyclohexanone (Chone) and peak-6 as toluene (T) and the mass spectra of these compounds are given in appendix (A1). The formation of toluene during catalytic reforming of n-heptane was reported by Beltramini et al.⁵³ on platinum supported on alumina (Pt/Al₂O₃), tin supported on alumina (Sn/ Al₂O₃), and platinum-tin supported on alumina (Pt-Sn/ Al₂O₃) catalysts. The other products formed were benzene and C₈⁺ aromatics. The reaction was carried out in hydrogen atmosphere (pressure = 5bar) at a temperature of 500°C. The yield of toluene was around 77% on Pt-Sn/ Al₂O₃ catalyst, around 15% on Sn/ Al₂O₃ and in case of Pt/Al₂O₃ catalyst the yield reached 60% and then it was found to decrease with increase in time. Pt/Al₂O₃ is a commercial hydroreforming catalyst and tin was added to it as it is known to enhance aromatization, inhibit hydrocracking and isomerization and decrease coke formation. The formation of toluene indicates that reforming also occurs during oxidation of n-heptane. The supported zirconium complex catalyst reported in this work gives one oxygenated product (Chone), the other products being isomer of hexane (2-MP), a dehydrocyclized

product of hexane (MCP), 4-M1-Ptene and an aromatized product of heptane (T) and there was no coke formation. From the analysis of the types of products formed we can conclude that n-heptane loses one carbon atom after which the latter undergoes isomerization, dehydrogenation and dehydrocyclization reactions and this results in the formation of 2-MP, 4-M1-Ptene and MCP. Generally the products formed on n-hexane reforming are 2-MP, 3-MP, MCP, 2,2-dimethylbutane (2,2-DMB) and 2,3-dimethylbutane (2,3-DMB) and benzene (B). On carrying out catalytic reforming of n-hexane using our catalyst the products formed were 2-MP, 3-MP, MCP and cyclohexane. It can also be concluded that n-heptane does not undergo direct oxidation giving its oxidation products but cyclohexane, formed when hexane gets dehydrocyclized, undergoes oxidation to form cyclohexanone. Stylkove et al.³² reported the formation of dienes (4-methyl-1,4-hexadiene and 2,4-dimethyl-1,3-pentadiene), heterocycles (2-methyl-5-ethyl-furan and 2,6 dimethyl-pyran), heptanones (2-, 3- and 4-heptanones) and 1-hepten-4-ol when n-heptane was partially air oxidized in presence of SAPO molecular sieves at 250°C and above. The reported conversion was 35.2% at 250°C and it increased with increase of temperature and excess of oxygen but there was also coke formation.

The effect of reaction time on conversion and product distribution was studied at 200°C. The variation of conversion with reaction time is shown in fig. 4.2.1. The conversion was 69% when the reaction was carried for 2 hours but it reached 79% for 8 hours of reaction time. The same products were formed for different reaction time and the variation in yield and selectivity with reaction time is given in fig. 4.2.2 and fig. 4.2.3 respectively. There was an increase in the yield of all the products with reaction time till 8 hours and for 8 hours reaction the yield of 2-MP, MCP, 4-M1-Ptene, Chone and T was

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4.99%, 5.25%, 12.36%, 25.7% and 23.35% respectively. For 12 hours reaction time there was an increase in the yield of 2-MP (21.5%) and MCP (10.24%) while there was a decrease in the yield of 4-M1-Ptene (11.47%), Chone (18%) and T (3.22%). There is a major decrease in the yield of T while the yield of 2-MP shows a major increase.

The effect of temperature on the conversion of n-heptane and the product distribution were studied in the temperature range of 160⁰C – 220⁰C keeping the total amount of oxygen fed as constant. The latter is achieved by putting an initial oxygen pressure of 100 psi in all experimental runs and the reaction time was 8 hours. The variation of conversion of n-heptane with reaction temperature is shown in fig. 4.2.4 and it can be seen that the conversion increases sharply for temperature greater than 180⁰C and is very high in the temperature range 200⁰C – 220⁰C (about 78%) while the conversion is only 18.57% at 180⁰C. The variation in yield and selectivity of the products formed with temperature is shown in fig. 4.2.5 and 4.2.6 respectively. At 200⁰C the yield of Chone is 25.7% and T is 23.35% which is the highest in the temperature range under study while at 160⁰C the yields of Chone and T are 2.12% and 0.79% respectively. At 220⁰C there is a slight decrease in the yield of T (21.82%) which is due to an increase in the cracking rate as the yield of the rest of the products is higher than that at 200⁰C.

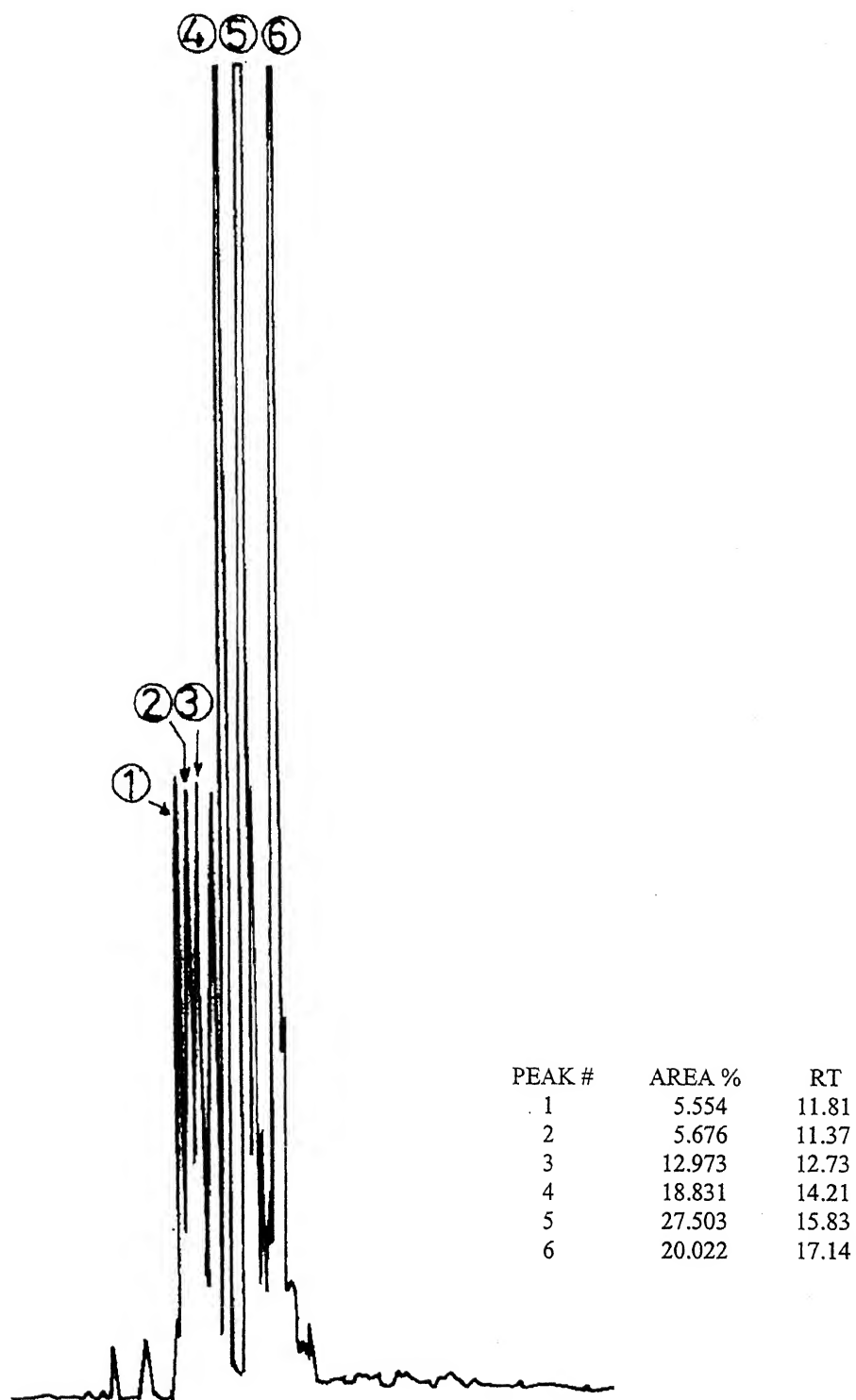


Figure 4.2 Gas chromatograph of the product formed on oxidation of n-heptane

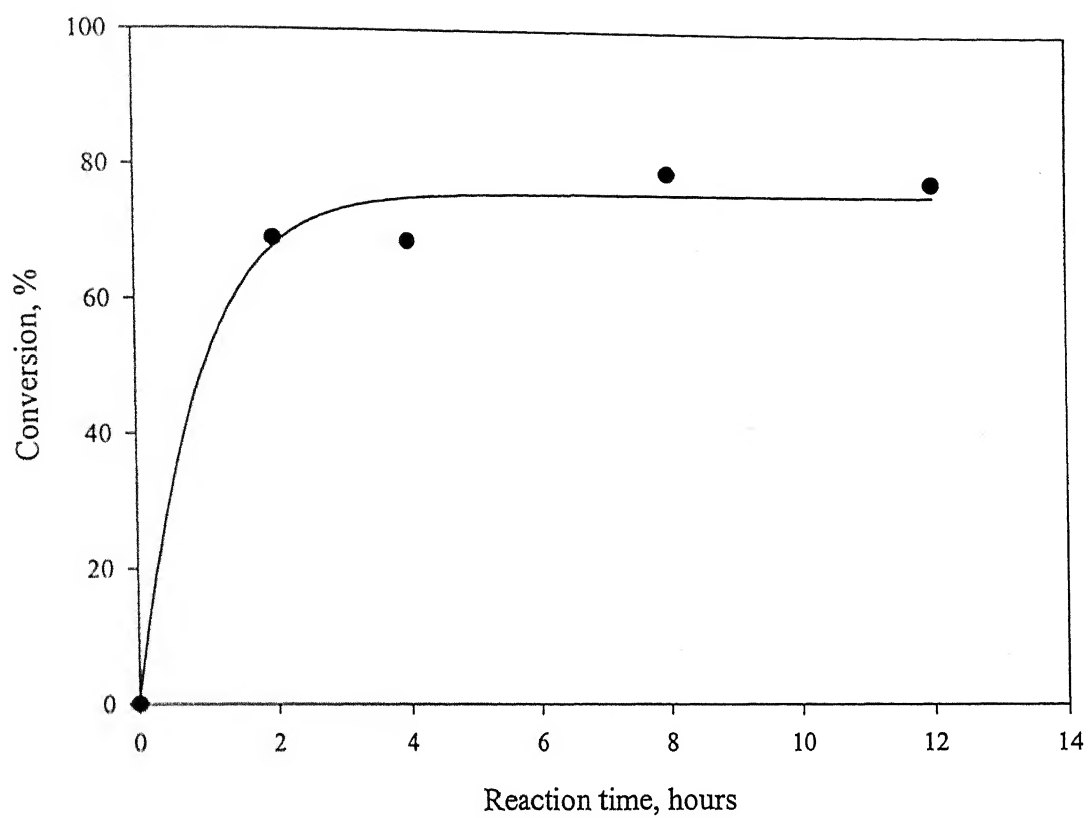


Figure 4.2.1 Effect of reaction time on the overall conversion of n-heptane

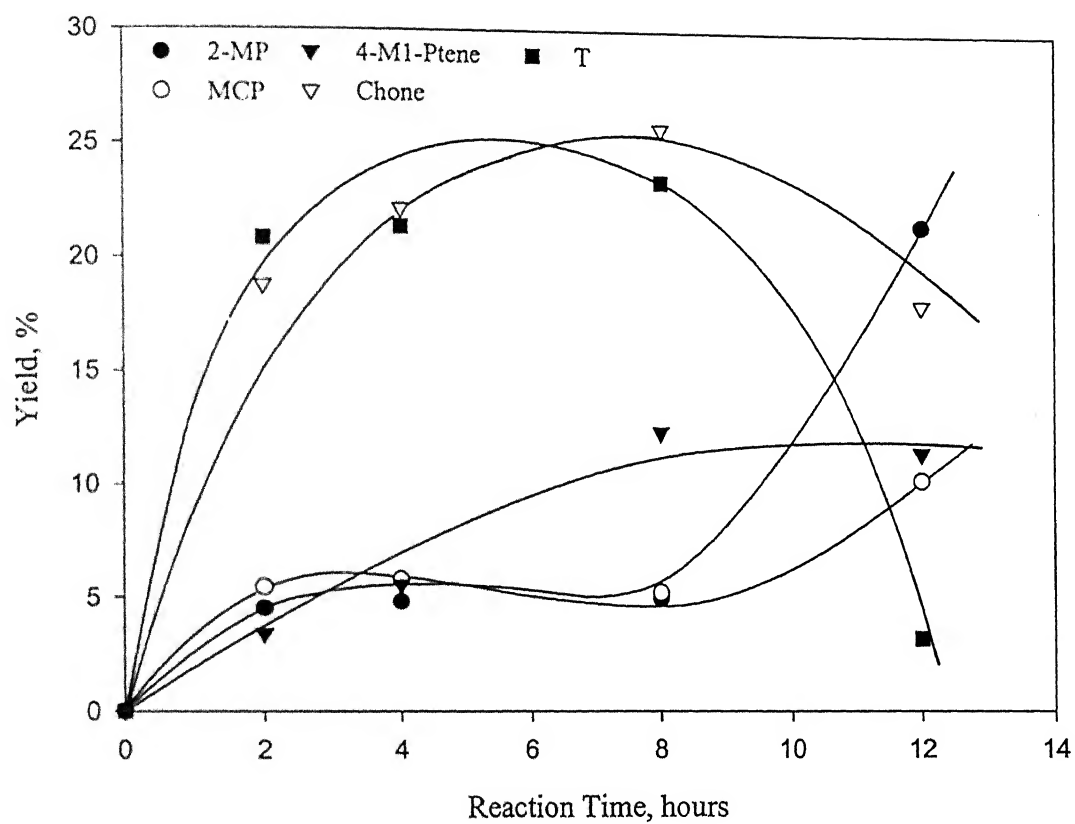


Figure 4.2.2 Effect of reaction time on the yield of the products formed on oxidation of n-heptane

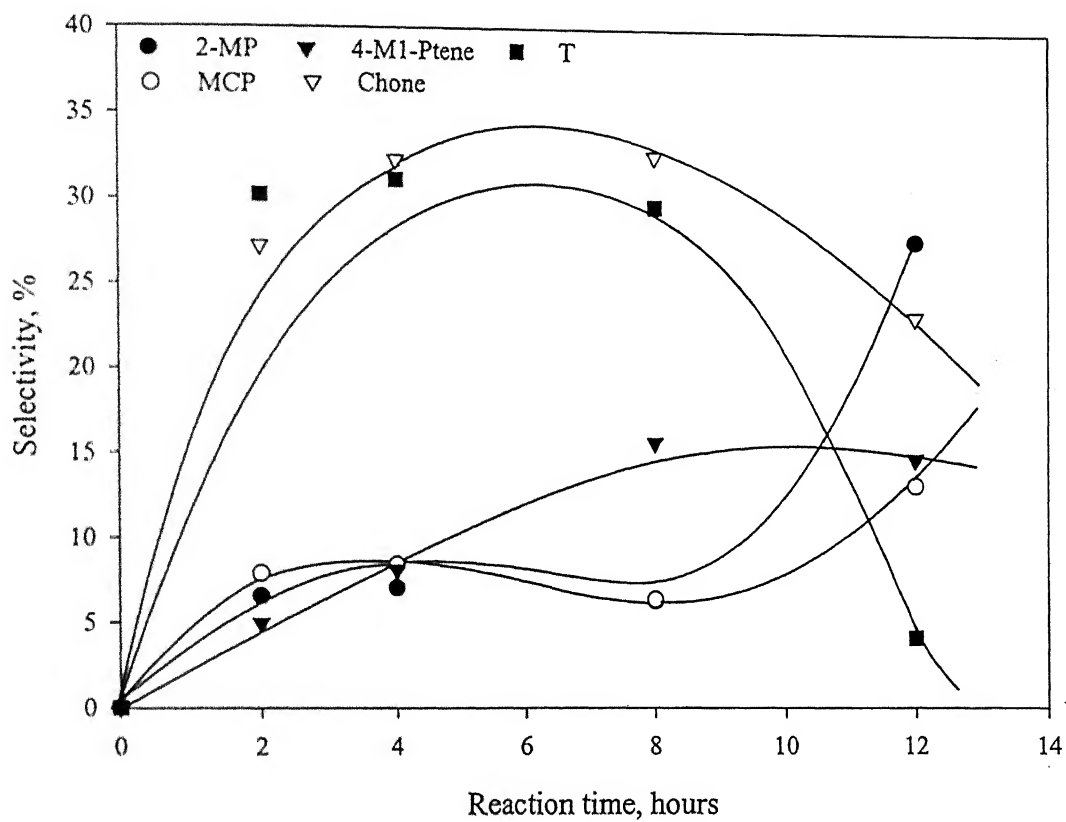


Figure 4.2.3 Effect of reaction time on the selectivity of the products formed on oxidation of n-heptane

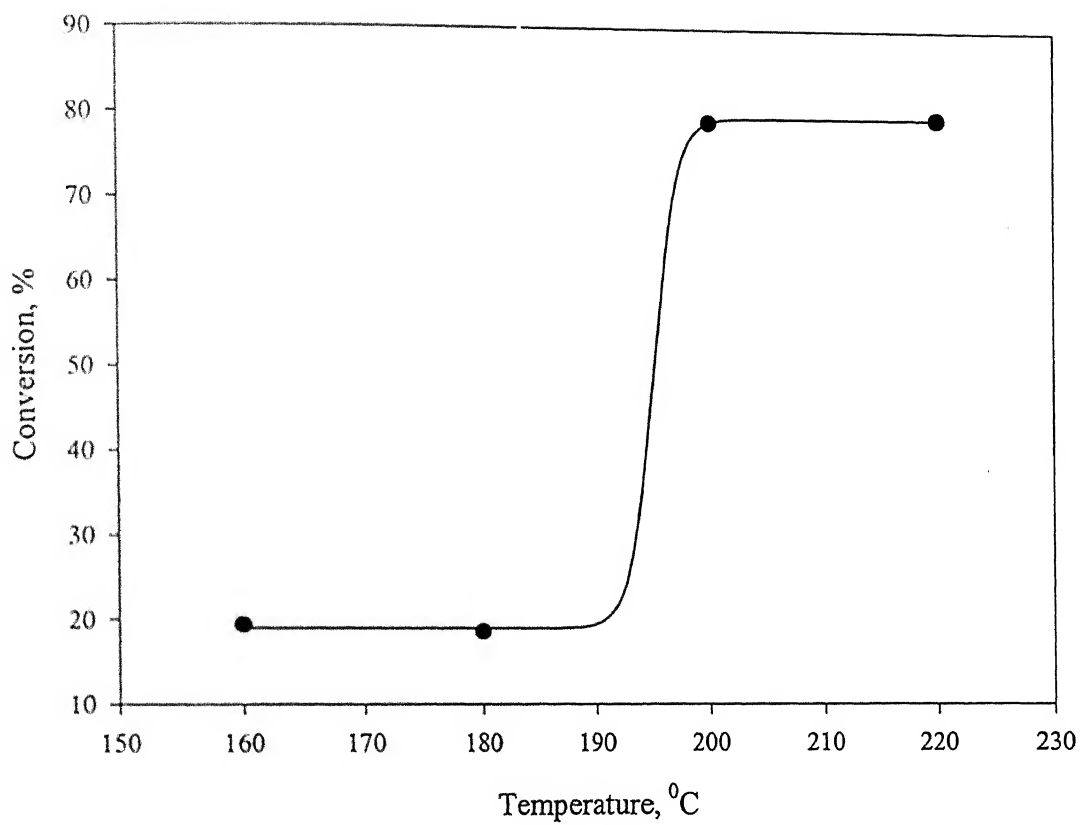


Figure 4.2.4 Effect of reaction temperature on the overall conversion of n-heptane

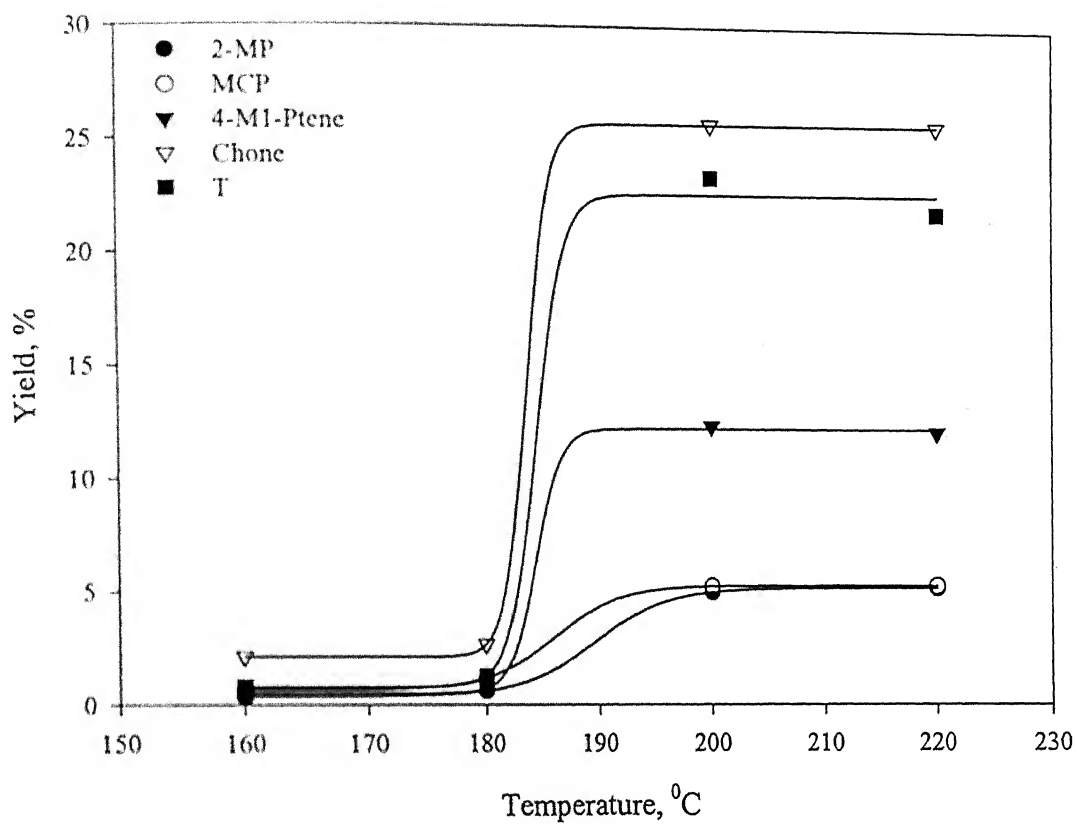


Figure 4.2.5 Effect of reaction temperature on the yield of the products formed on oxidation of n-heptane

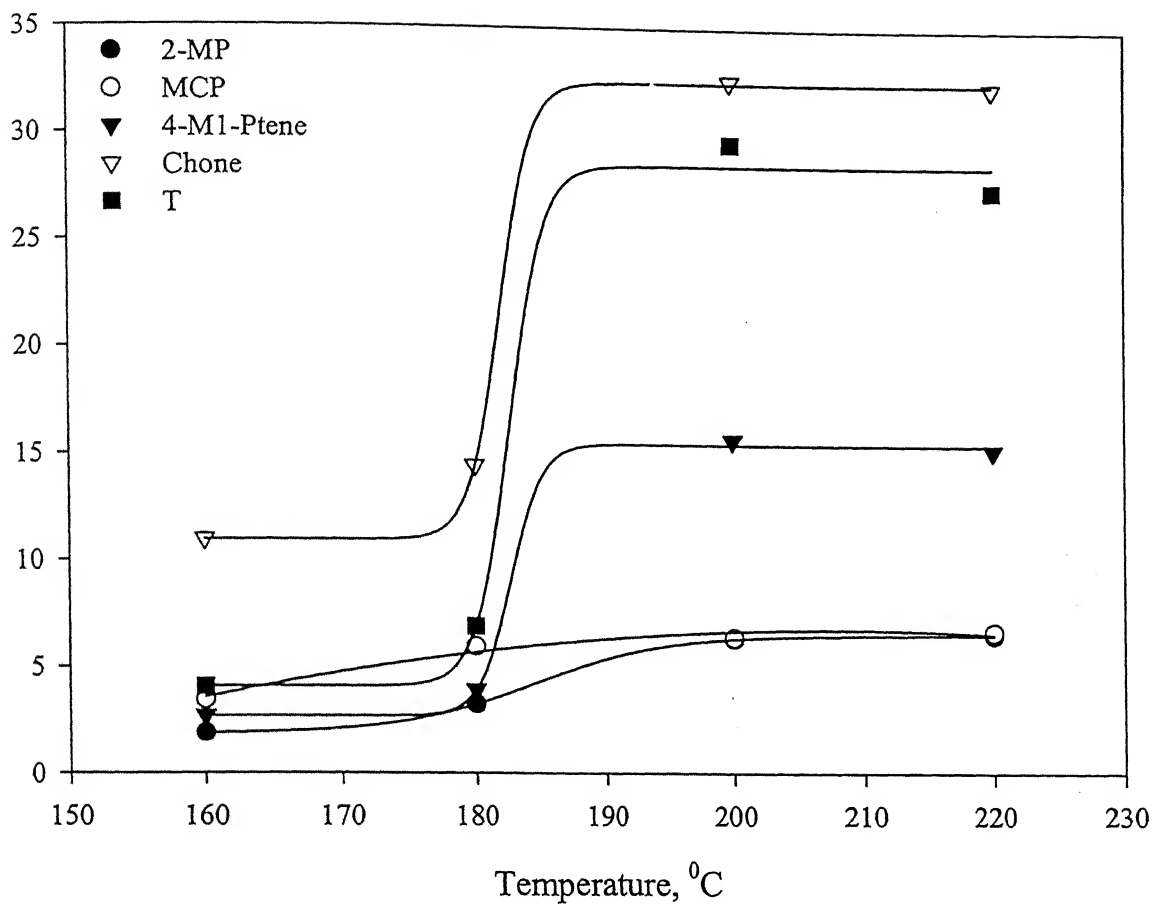


figure 4.2.6 Effect of reaction temperature on the selectivity of the products formed on oxidation of n-heptane

4.3 Oxidation of cyclohexane in presence of molecular oxygen

The oxidation of cyclohexane was studied in a batch reactor by keeping the mass of the catalyst constant (1g) at different temperatures (between 120⁰C and 200⁰C) and for different reaction period (between 2 to 12 hours). For the product of one of the runs (at 200⁰C temperature, 100psig oxygen pressure and 8 hours of reaction time), fig. 4.3 shows the gas chromatograph (GC) giving a total of 3 peaks. The identification of the compounds has been done by the mass spectra of the compounds corresponding to the peaks in the GC and matching them with those given in literature. Peak-1 has been identified as cyclohexane (CH), peak-2 as cyclohexanol (Chnol) and peak-3 as cyclohexene (Chene) and the mass spectra of these compounds are given in appendix (A1). The catalytic system currently in use for industrial cyclohexane oxidation employs homogeneous cobalt salts, molecular oxygen and temperatures above 150⁰C, with conversion around 4% and selectivity of 85% to a mixture of cyclohexanone and cyclohexanol ⁵⁶. The heterogeneous catalysts, which have been investigated, are either oxides or metal cations and complexes incorporated on inorganic matrices such as silica, alumina, zirconia, active carbon, zeolites or aluminophosphates ⁵⁷. The activity of the heterogeneous catalytic system also depends on the correct choice of the solvent, which determines the polarity of the medium, however there is a disadvantage of metal leaching. For example during the oxidation of cyclohexane in presence of CoAPO-5, catalyst the use of carboxylic acid (except formic acid) as the solvent is necessary and the use of propionic acid results in the highest reaction rate at a

temperature below 135°C ³⁵. In case of cyclohexane oxidation there is an induction time which is reduced by adding promoters or coreactants such as acetaldehyde, cyclohexanone, cyclohexanol and azobiz(isobutyronitrile) (AIBN). Coreactants also helps in increasing the rate of cyclohexane oxidation (decreases the apparent activation energy) and selectivity of the target products (cyclohexanone, cyclohexanol). Generally cyclohexanol and cyclohexanone are formed in comparable amount along with acids like butyric acid, valeric acid etc which are undesirable ⁵⁸. For example in the oxidation of cyclohexane using molecular oxygen catalyzed by cobaltous palmitate loaded on modified polymer support, cyclohexanol and cyclohexanone were formed in the ratio of 1.6:1 ³⁶. In our case, at 200°C , in presence of supported zirconium complex catalyst cyclohexanol was the main product along with small amounts of cyclohexene and the oxidation is carried out in the absence of coreactant and solvent.

The conversion and product distribution as a function of reaction time was studied by keeping the initial oxygen pressure (100 psig) and reaction temperature (200°C) fixed. Fig 4.3.1 shows the variation of conversion of cyclohexane with reaction time and it is found to increase with increase in reaction time. For 12 hours reaction time the conversion reached 23.4% while it was only 10.3% for 2 hours reaction time. Fig 4.3.2 and 4.3.3 shows the variation in yield and selectivity respectively with reaction time. In the reaction period of 4 hours to 12 hours cyclohexanol was obtained as the major product together with small amounts of cyclohexene. In this reaction period the selectivity of cyclohexanol was around 72.5% and the yield of cyclohexanol increases with increase in reaction time. For 12 hours reaction time the yield of cyclohexanol and cyclohexene were 17.039% and 2.93% respectively. When the reaction was carried out for 2 hours cyclohexanol was not

formed and cyclohexene was the main product, the yield and selectivity of cyclohexene being 8.021% and 77.9% respectively.

The effect of temperature on the conversion as well as the product distribution was studied by keeping the initial oxygen pressure (100 psig) and reaction time (8 hours) constant. As seen from fig 4.3.4 the conversion is found to increase with increase in reaction temperature. At 120⁰C the conversion was only 1.03% while at 200⁰C the conversion reached 21.37%. The variation in yield and selectivity with increase in reaction temperature is shown in fig 4.3.5 and 4.3.6 respectively. Significant amount of products are formed only in the temperature range 170⁰C – 200⁰C, the major product being cyclohexanol together with small amounts of cyclohexene. At 120⁰C the products are formed in very small amount as a result of which the peaks do not appear in the GC.

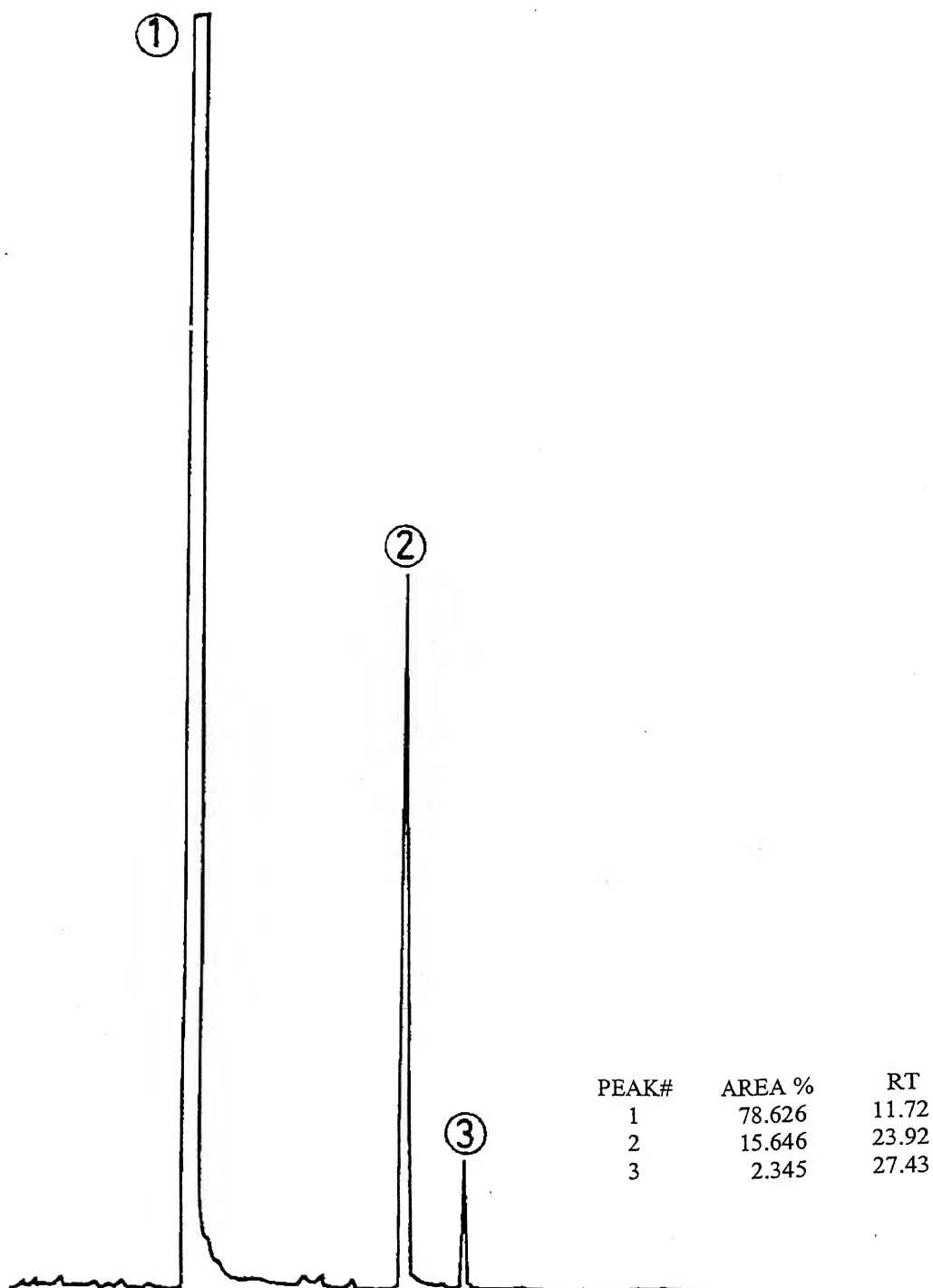


Figure 4.3 Gas chromatograph of the product formed on oxidation of cyclohexane

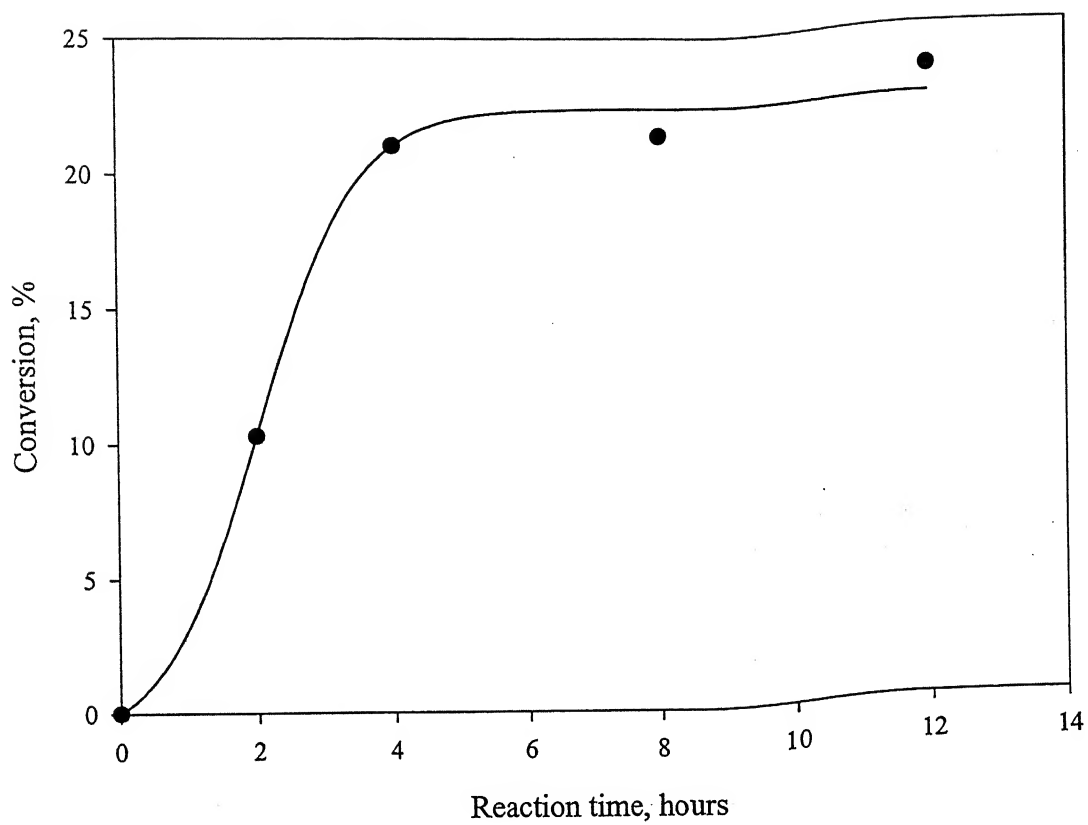


Fig 4.3.1 Effect of reaction time on the overall conversion of cyclohexane

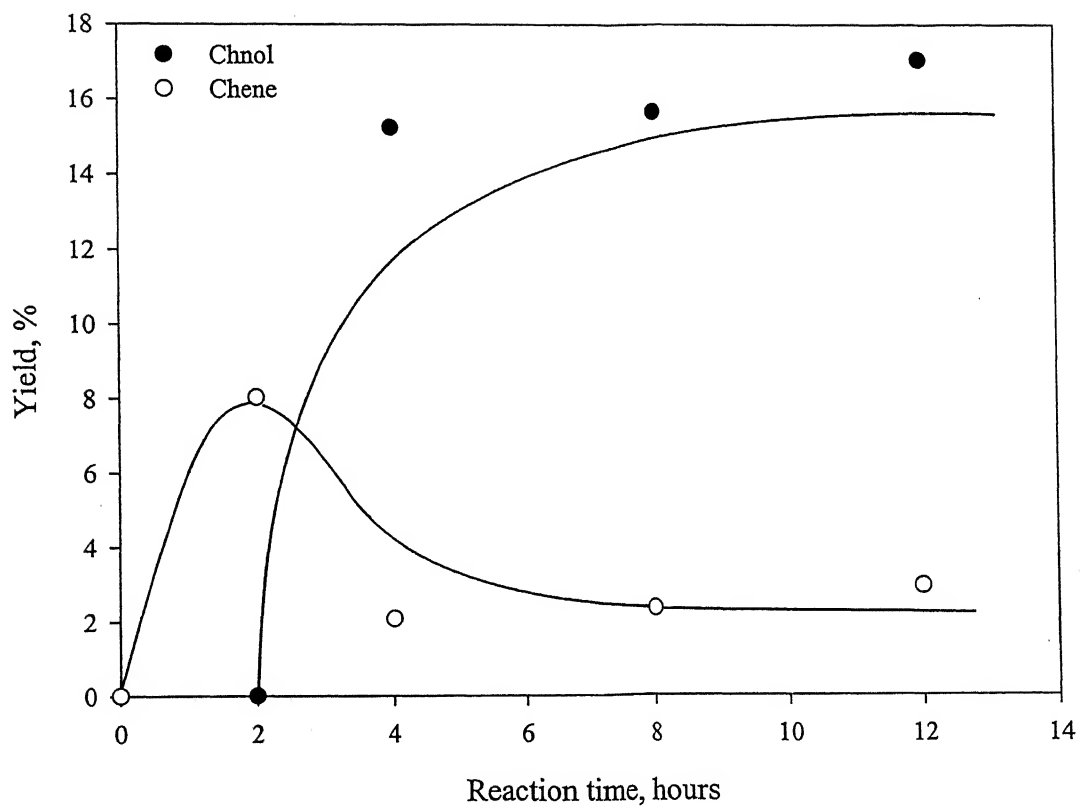


Figure 4.3.2 Effect of reaction time on the yield of the products formed on oxidation of cyclohexane

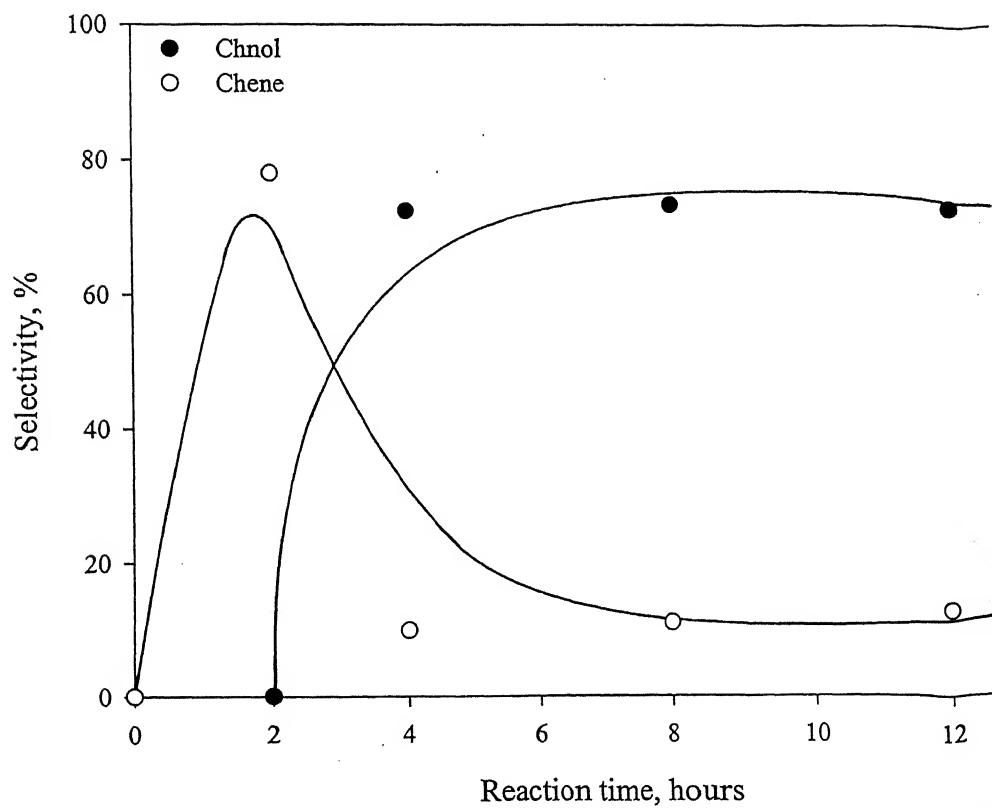


Figure 4.3.3 Effect of reaction time on the selectivity of the formed on oxidation of cyclohexane

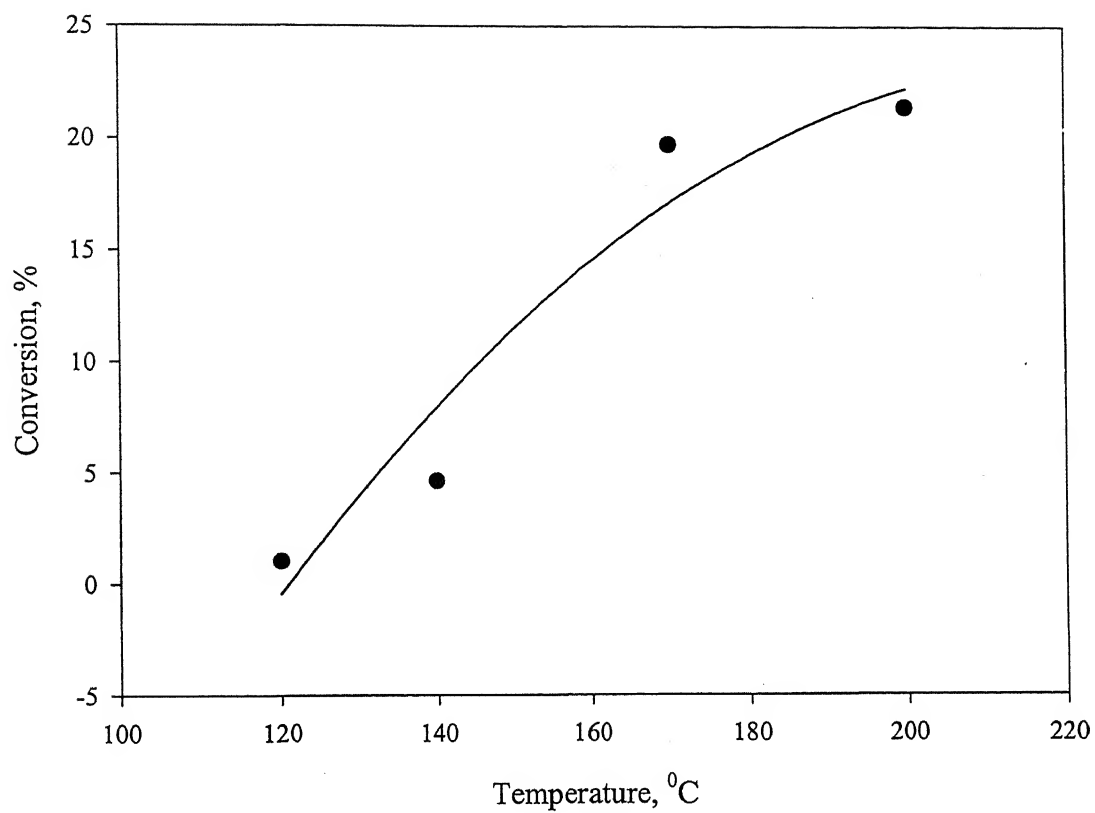


Figure 4.3.4 Effect of reaction temperature on the overall conversion of cyclohexane

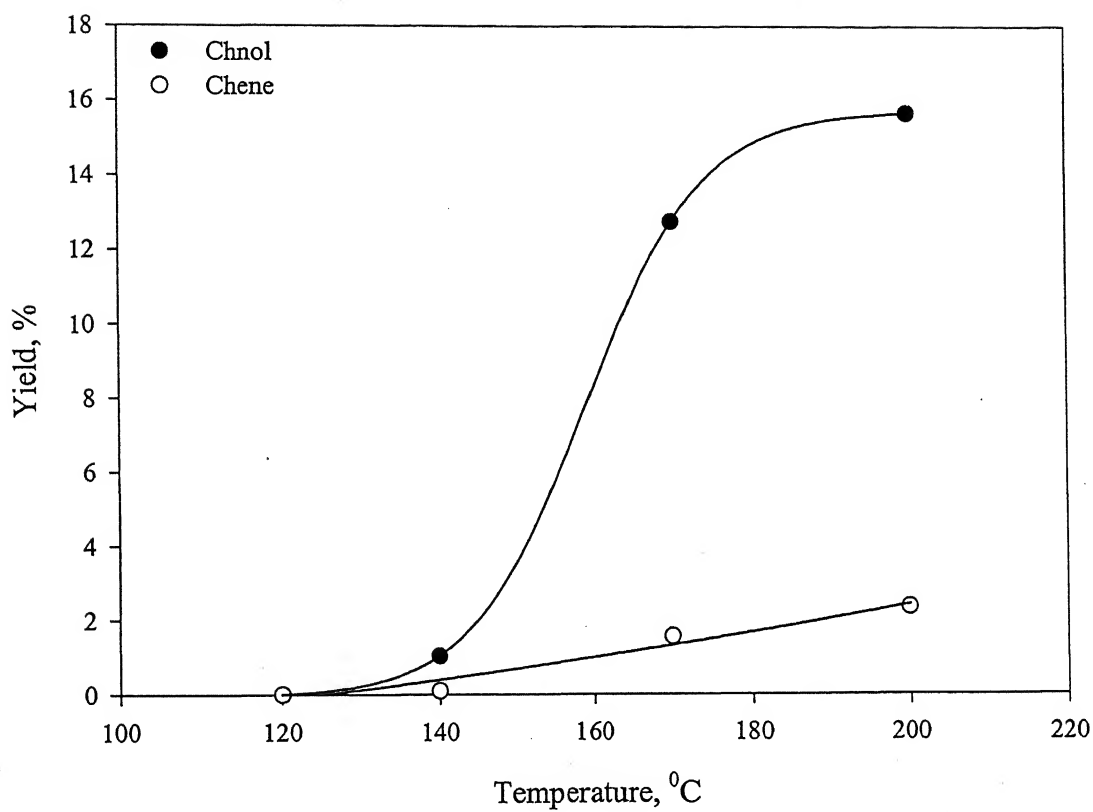


Figure 4.3.5 Effect of reaction temperature on the yield of the products formed on oxidation of cyclohexane

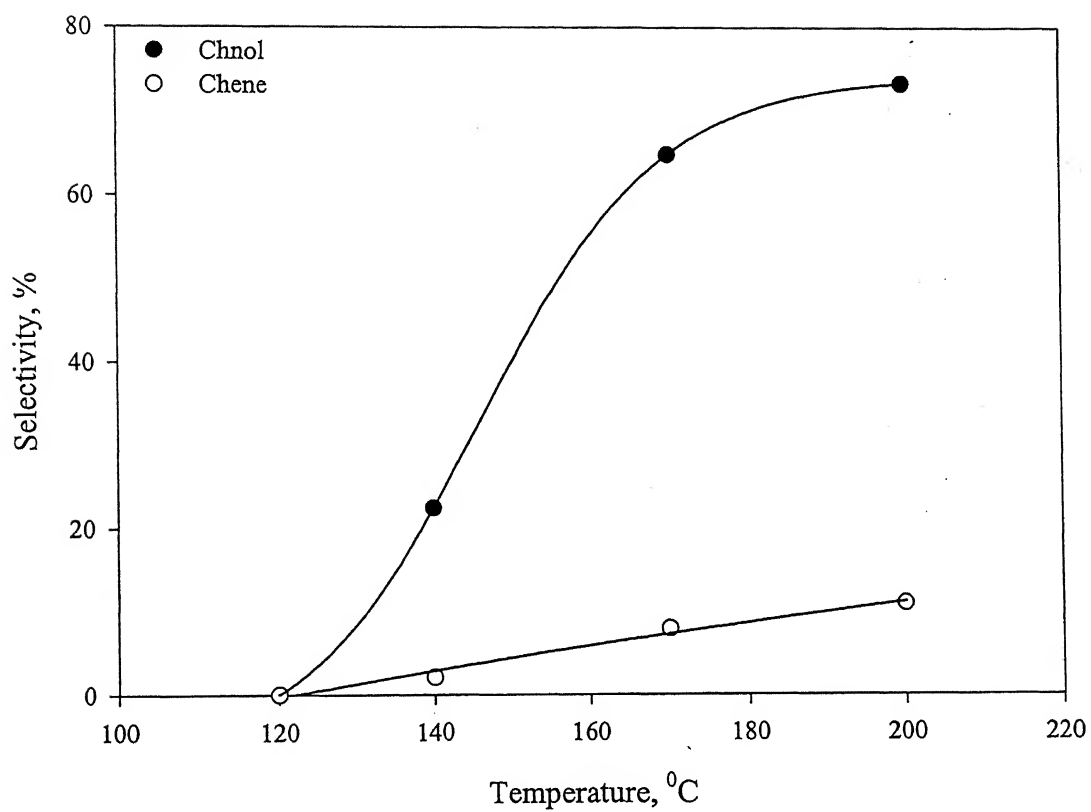


Figure 4.3.6 Effect of reaction temperature on the selectivity of the products formed on oxidation of cyclohexane

4.4 Depolymerization of HDPE

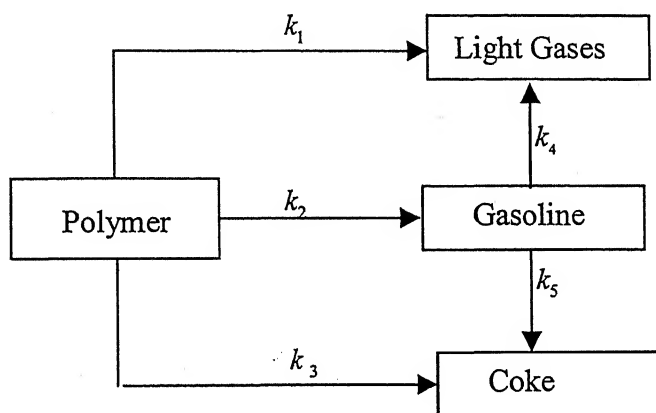
The depolymerization of HDPE has been studied in a batch reactor in presence of the modified alumina supporting zirconium complex catalyst in nitrogen environment. The HDPE to catalyst ratio used was 10:1 and the reaction was conducted at 335°C for six hours. Solid, liquid and gaseous products were formed and their % yield was found to be 12.5%, 63.5% and 25% respectively. The liquid products comprised mainly of straight chain alkanes from C₇ to C₁₅, their percentage (in the liquid product) is given in table 4.4 and fig 4.4 gives the chromatogram. The experiment was duplicated and the repeatability of the result was within $\pm 1.00\%$ for product yield. The life of the catalyst was tested by using the catalyst repeatedly and the yield of the products were found to remain the same. The depolymerization of the HDPE reported in literature normally occurs in the temperature range 400°C – 500°C. Strong acid catalysts such as HZSM-5 (zeolite), metals (Pt, Ni etc) incorporated on sulfated zirconia have been used and the catalytic activity is due to their ability to cleave carbon bonds. The FCC (zeolite) and reforming catalysts (Pt/Al₂O₃) are used in depolymerizing HDPE and they show higher selectivity towards aromatics and naphthenes. The oil products formed in presence of HZSM-5 were olefins, n-paraffins, aromatics, naphthenes and others (I-paraffins, cyclic- olefins). The main reactions in presence of HZSM-5 was assumed to

n-paraffins → naphthenes

olefins → aromatics

cyclo-olefins → aromatics + naphthenes

In case of complex feed stocks (bovine waste, black liquor, wood coal etc) the different products obtained are lumped into groups. For example, Shafizadeh et al. have proposed a model for wood pyrolysis in which various products are lumped into 3 groups viz. gas tar and char. In their model, the wood is pyrolyzed into gas, tar and char from three parallel reactions and the tar further decomposes into gas and char. Similar lumping techniques have also been used to develop kinetic models for catalytic cracking of plastics. Lin et al. adopted a lumped model for catalytic depolymerization of HDPE and PP over zeolite catalyst and the model can be represented as



With the catalyst reported in this work depolymerization is found to occur at a very low temperature (335°C) in the absence of initial pressure.

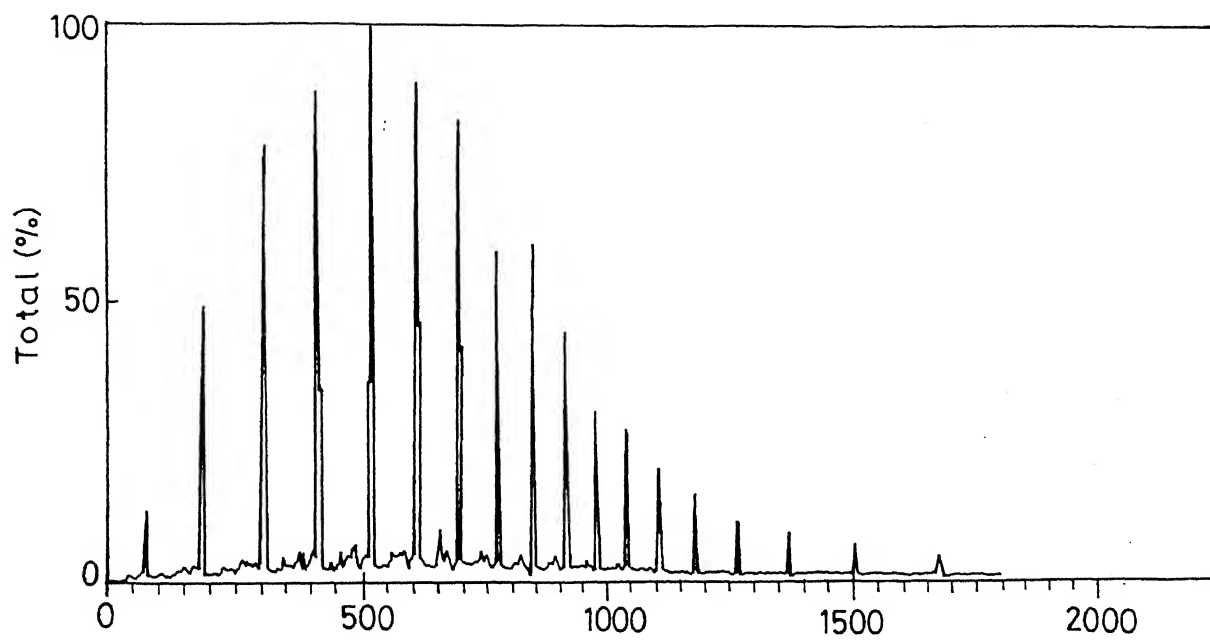


Figure 4.4 Chromatogram of the liquid product formed on depolymerization of HDPE

Table 4.4 Liquid product analysis on depolymerization of HDPE

Serial number	Carbon number	%Total
1	C ₇	1.80
2	C ₈	6.00
3	C ₉	9.50
4	C ₁₀	22.90
5	C ₁₁	11.20
6	C ₁₂	9.50
7	C ₁₃	8.40
8	C ₁₄	10
9	C ₁₅	9.7

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

We have synthesized a zirconium metal complex and molecularly bound it to the modified carbamate silica gel and alumina supports. The heterogeneous catalyst thus prepared has been used for reactions of alkanes.

1. During the catalytic reforming of n-hexane, isomerized products (2-MP, 3-MP) and dehydrocyclized products (MCP, CH) were formed and the yield of the isomerized products was higher than the yield of the dehydrocyclized products in the temperature range ($120^{\circ}\text{C} - 190^{\circ}\text{C}$) under study. As opposed to this, the commercial reforming catalyst ($\text{Pt}/\text{Al}_2\text{O}_3$) works in the temperature range of $350^{\circ}\text{C} - 550^{\circ}\text{C}$ and forms four isomerized products (2-MP, 3-MP, 2,2-DMB, 2,3-DMB), dehydrocyclized products (MCP and CH) and aromatic (B).
2. With this catalyst, in the conversion-time study, the reaction seems to have approached equilibrium in less than 2 hours and the conversion of n-hexane was less sensitive to temperature in the studied temperature range.
3. In the oxidation of n-heptane using our catalyst ($160^{\circ}\text{C} - 220^{\circ}\text{C}$), cyclohexanone is the only oxygenated product formed and the rest being toluene, 4-methyl,1-pentene C_6 isomer (2-MP) and a dehydrocyclized product MCP. The commercial oxidation catalyst is SAPO molecular sieve ($250^{\circ}\text{C} - 550^{\circ}\text{C}$) and gave a mixture of furans, pyrans and heptanones

4. At and above 200⁰C the conversion of n-heptane shows a major rise (79%) with high selectivity for cyclohexanone (32%), toluene (27%), 4-methyl,1-pentene (15%), methylcyclopentane (6%) and 2-methylpentane (6%). As opposed to this the commercial catalyst gave an overall conversion of 35%.
5. The conversion of n-heptane increases with increase in reaction time. For 12 hours reaction time the yields of cyclohexanone and toluene decreases while for rest of the products, the yield increases.
6. During the solvent free oxidation of cyclohexane significant reaction occurred only above 170⁰C giving a conversion of ~20% which is very high when compared with the commercially used process catalyzed by homogeneous cobalt salts (conversion of 4%, at 150⁰C, propionic acid as solvent and cyclohexanone as coreactant).
7. Cyclohexanol was obtained as the main product (72% selectivity) alongwith small amounts of cyclohexene (11% selectivity) and this demonstrates high specificity of the catalyst. Several unidentified products (17% selectivity) were also formed, which may be regarded as waste. As opposed to this, the commercial catalyst gives cyclohexanol (52% selectivity), cyclohexanone (33% selectivity) and waste products (15% selectivity, consisting of butyric acid, valeric acid, cyclohexyl adipate).
8. The conversion of cyclohexane shows only a slight increase when the reaction time is increased beyond 4 hours. There is a major increase (~11% increase) in conversion when the reaction time is increased from 2 hours to 4 hours and there is no induction time.
9. On depolymerization of HDPE using our catalyst (nitrogen atmosphere, at 335⁰C) the liquid products obtained comprised mainly of n-alkanes in the range C₇ – C₁₅. As

opposed to this, in presence of zeolite catalyst the liquid products formed comprised of aromatics, n-alkanes, i-alkanes and naphthenic products.

5.2 Recommendations

The following recommendations are proposed for further study

1. Catalytic reforming of n-hexane should be studied at higher temperatures (300°C – 400°C) and check whether cyclohexane further gets converted to benzene or not. Oxidation of n-hexane should also be studied.
2. Isomerization of light alkanes (butane and pentane) should also be studied.
3. The gaseous products obtained during HDPE depolymerization should also be analyzed and identified.
4. Depolymerization of HDPE should be studied for higher temperatures (upto 430°C) and for different reaction time.
5. The effect of reaction time on the product distribution and yield should also be studied for HDPE depolymerization.

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Appendix A1

Mass spectra of organic compounds obtained by mass spectroscopy analysis of the products and matched with literature.

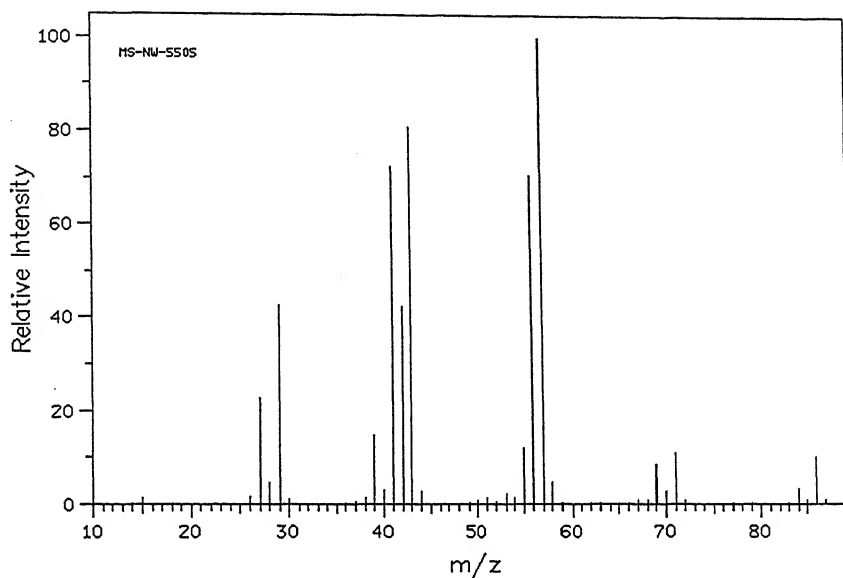


Fig A1.1 Mass Spectra of n-Hexane

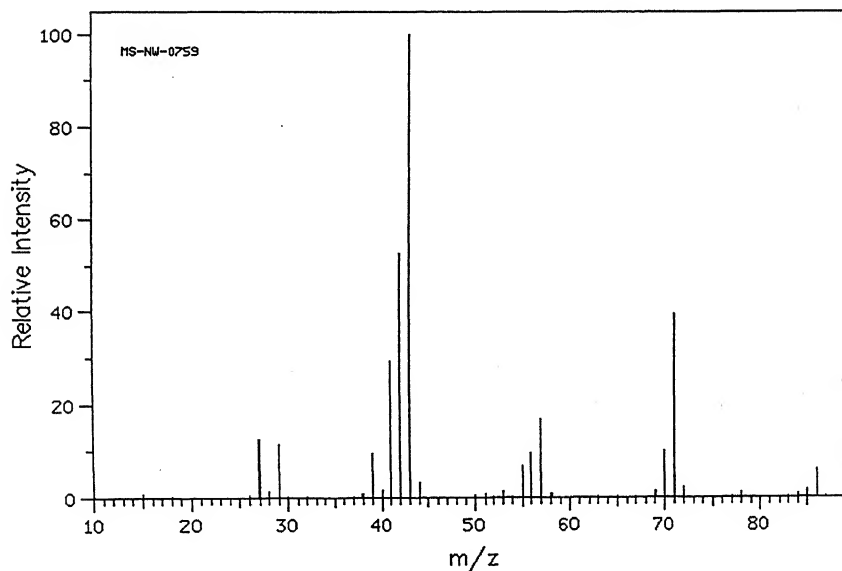


Fig A1.2 Mass Spectra of 2-Methylpentane

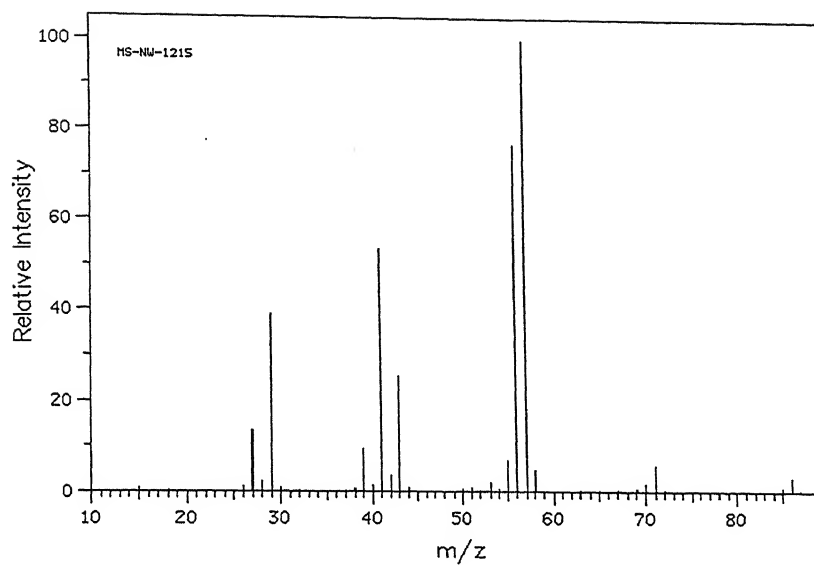


Fig A1.3 Mass Spectra of 3-Methylpentane

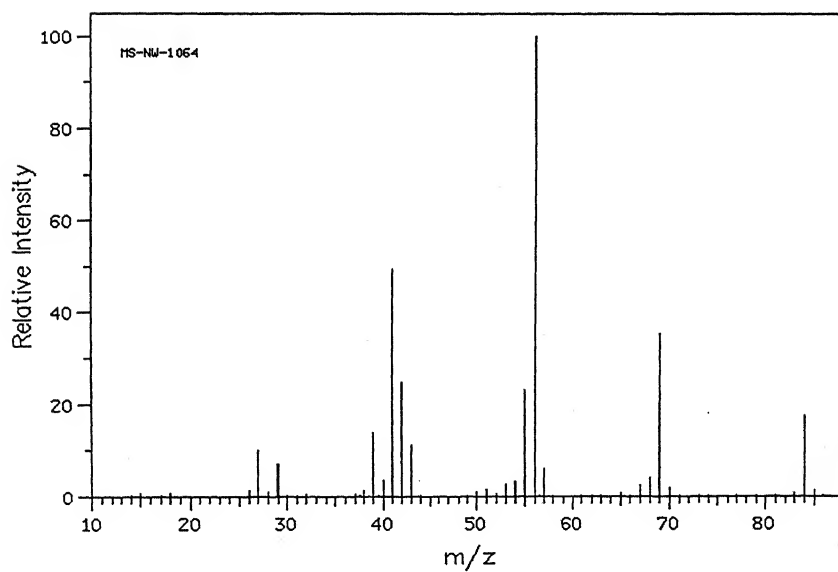


Fig A1.4 Mass Spectra of Methylcyclopentane

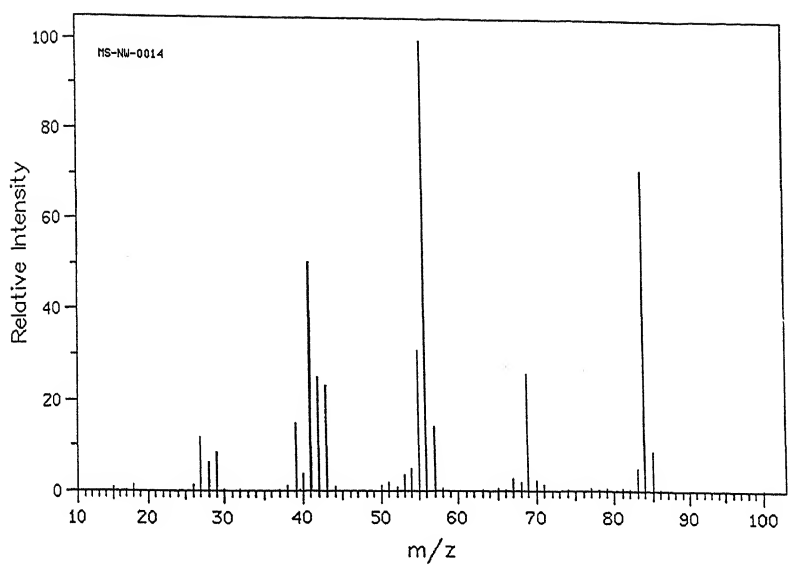


Fig A1.5 Mass Spectra of Cyclohexane

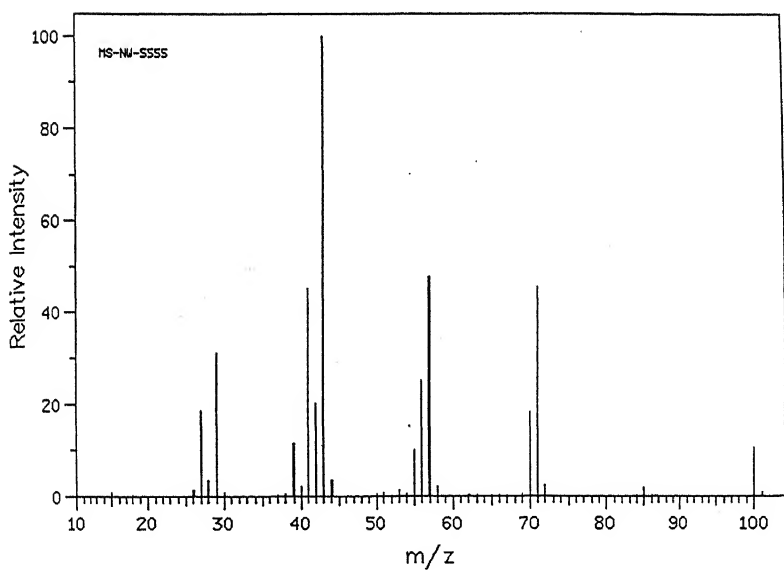


Fig A1.6 Mass Spectra of n-Heptane

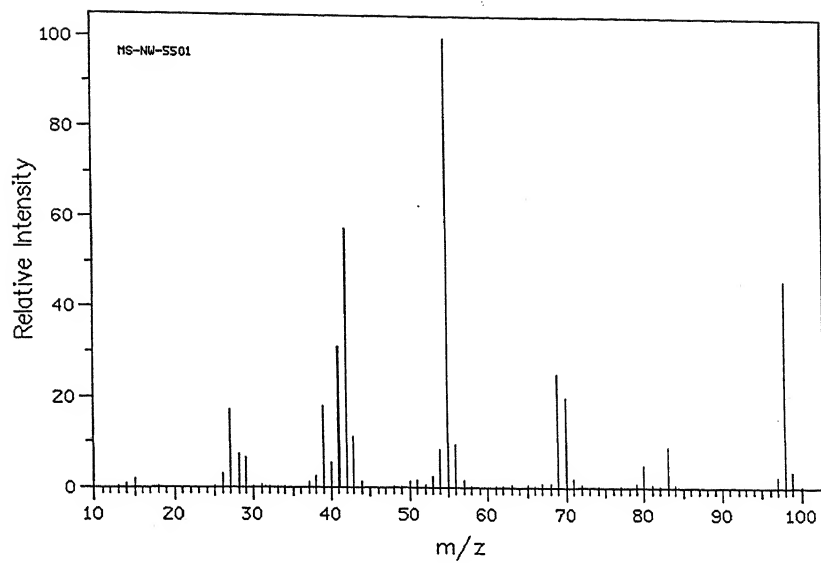


Fig A1.7 Mass Spectra of Cyclohexanone

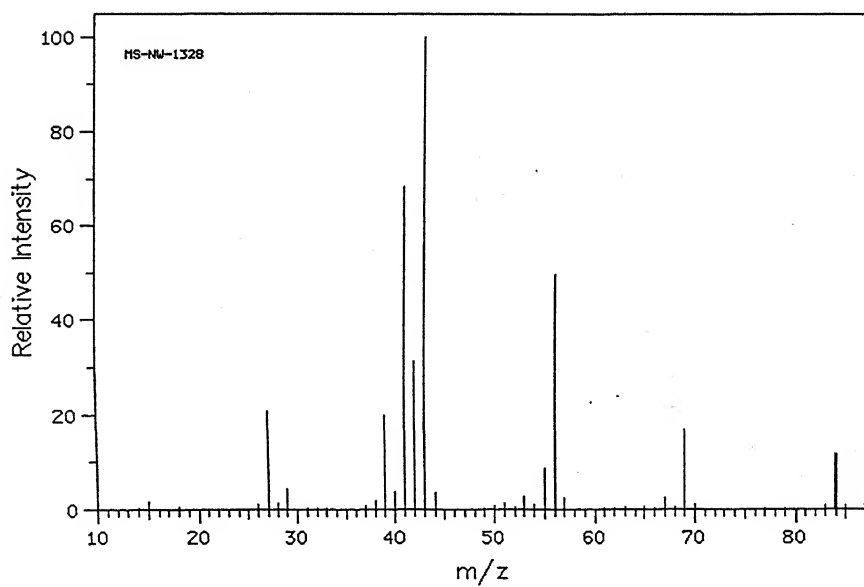


Fig A1.8 Mass Spectra of 4-Methyl,1-pentene

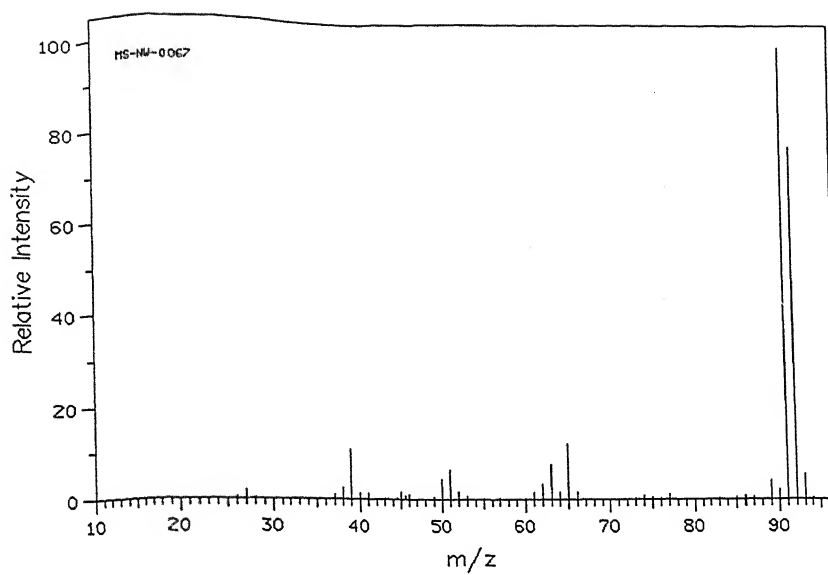


Fig A1.9 Mass Spectra of Toluene